N00164.AR.000572
NSWC CRANE
5090.3a

Work Plan
for
Risk Assessment
at
SWMUs 4, 5, 9, and 10

Naval Surface Warfare Center
Crane Division
Crane, Indiana

VOLUME III - LABORATORY SOPs

Southern Division
Naval Facilities Engineering Command
Contract Number N62467-94-D-0888
Contract Task Order 0010

August 2000

LABORATORY SOPs

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• LTL-1004	4	Documentation of Analyst Competence and Training
• LTL-1005	5	Analytical Balances
• LTL-1006	3	Refrigerator, Freezer, and Oven Thermometer Calibration and Maintenance
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• LTL-1009	2	Blind Spike Program
• LTL-1011	4	Procedures for the Determination and Reporting of Detection Limits, Reporting Limits, Precision and Accuracy Studies, and Control Limits
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• LTL-1020	1	Integration of IC, GC, HPLC and GCMS Peaks
• LTL-2001	5	Waste Segregation and Disposal
• LTL-3000	11	Extraction Method for Base, Acid, and Neutral Compounds in Water (8270 C by 3520C).
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• LTL-3161	4	Extraction Method for Ordanance Compounds in Soils
• LTL-3202	2	Extraction Method for Organochlorine Pesticides and Polychlorinated Biphenyls in Water (8081A/ 8082 by 3510C)
• LTL-3302	2	Extraction Method for Organochlorine Pesticides and Polychlorinated Biphenyls in Soil (8081A/ 8082 by 3550B)
• LTL-3450	1	Extraction Method for Polynuclear Aromatics in Soil (8270C by 3550B)
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• LTL-7015	1	Acid Digestion of Sediments, Sludges, and Soils Using SW 846 Method 3050B
• LTL-7101	3	Operation of the Jarrell-Ash Enviro36 Simultaneous ICP
• LTL-7105	1	Method Protocols for the Analysis of Metals by ICP Using SW 846 6010B
• LTL-7202	4	Metals Analysis Using Inductively Coupled Plasma - Mass Spectrometry (ICP/MS) SW846 Method 6020
• LTL-7501	1	Operation of the PE FIMS 400 for the Analysis of Hg
• LTL-8000	1	Determination of Retention Time Windows
• LTL-8019	3	Determination of Non-Halogenated Volatile Organics by Method SW 8015B
• LTL-8084	3	Analysis of Organochlorine Pesticides and PCBs by SW 846 Methods 8081A and 8082
• LTL-8151	2	Analysis of Chlorinated Herbicides by Method 8151A
• LTL-8265	2	Determination of Volatile Organic Compounds bySW 846 Method 8260B
• LTL-8276	2	Determination of Semivolatile Organic Compounds by SW-846 Method 8270C
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• LTL-8330	10	Determination of Nitroaromatics and Nitramines by SW-846 Method 8330
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• LTL-9113	2	pH in Soil and Waste Samples Using SW 846 Method 9045C
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• LTL-9125	1	Nitrate/Nitrite as N by Lachat
• LTL-9202	2	Total Suspended Solids (Non-filterable Residue) Using EPA Methods 160.2/Standard Method 2540D and Total Volatile Suspended Solids Using Standard Methods 2540E
• SM-2340B	0	Hardness Calculation
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• 2.04	3	Non-Conformance
• 5.01	8	Sample Receipt, Identification, Handling, and Storage
• CQA125	3	Establishing Method Detection Limits
• DHR182	6	PCDDs and PCDFs by HRGC/HRMS - Method 8290
• DPA104	12	Data Package Assembly and Shipping
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• DSP260 [1]	5	SLICC III - Acid Aluminum
• DSP270 [1]	2	Preparing, Cleaning, and Activating Column Packings for Cleanup
• SMC114	2	Creating the TLI Chain of Custody
• SMC120	1	Sample Storage and Handling

[1] These SOPs are company confidential and do not appear in this appendix. These SOPs have already been submitted to EPA under CTO 38.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1001

Title: **Elements of SOP and Method Formats**

Revision history:

Number	Date
4	5/3/99
3	7/22/94
2	9/16/87
1	7/31/86

Written by: Harry Romberg
Harry Romberg, QA Officer
Date: 5-3-99

Approved by: Kathy Kreps
Kathy Kreps, Laboratory Director
Date: 5-6-99

Controlled Document
No. 20 Assigned to: Tetra

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1. Introduction and Scope

1.1 Purpose

1.1.1 The purpose of this SOP is to define the process of creating SOPs and Methods.

1.2 Scope

1.2.1 SOPs are considered to be administrative and other non-analytical tasks.

1.2.2 Methods are considered to be technical analytical procedures and are generally derived from EPA or other analysis methods. Both have similarities and differences in structure and necessary elements. This document assumes that the user either has some knowledge of the word processor being used or can figure out how to perform the basic operations necessary.

1.2.3 This SOP does not address document control except as it relates to numbering of the SOP. Document control is addressed in Laucks SOP LTL-1002.

2. Procedures

2.1 Word Processing Format

2.1.1 All new SOPs are written in WORD 6 format (or higher when accepted by QA). Older versions of SOPs may be written in WORD 2 or XyWrite, however, these formats should be updated to meet the current format as they are revised.

2.1.2 Flow charts may either be photocopied from methods, scanned and inserted into the document electronically or prepared from programs such as Flow 4 (Patton & Patton Software) and inserted into the document electronically. Any of these electronic files should be kept together with the electronic version of the document to facilitate its modification and inclusion into future updates.

2.2 Initiating an SOP or Method

2.2.1 Prior to creating a new SOP or Method or revising an existing document, the prospective author or supervisor should first complete a Document Control Form as specified in the document control SOP, LTL-1002. This form can be obtained from the QA Department.

2.2.2 SOPs are considered to be administrative and other non-analytical tasks. Methods are considered to be technical analytical procedures and are generally derived from EPA or other analysis methods. For tracking and control purposes, all will be assigned a number by the QA Officer or designee. This number will begin with the letters LTL- (such as this

SOP, LTL-1001). A number should be obtained from QA before the author begins writing the SOP but if this is not possible, a number must be obtained before the SOP can be turned in for review.

2.2.3 If a revision of a previous document is being undertaken, the SOP or Method number will remain the same but the revision number will be incremented. Revision numbers of new documents will automatically be assigned as 0 with subsequent revisions generally being incremented by 1 (1, 2, 3, etc.).

2.2.4 The author may then use the appropriate Word template (SOPhead, Iorgtemp or Orgtemp) from the [File][New] menu presented in Word. Hardcopies of these formats are not included in this SOP but may be accessed by the reader using the above means. These formats may change somewhat without updating of this SOP but if the author accesses the template from the laboratory network in this manner, the latest version will be automatically used.

2.2.5 These are meant for guidance only and changes to the formats will be allowed if they present a more complete and accurate account of method performance. While it is entirely up to the author to change any part of one of these templates to suit the specific procedure, these elements will be looked at in the review process and must be included unless they are inappropriate to the procedure being described.

2.2.5.1 **SOPhead** is a general SOP template. This template is NOT to be used for analytical methods as it does not contain all of the necessary elements of a method (i.e. QC requirements). Specific elements of a method are outlined below and in the method templates Iorgtemp and Orgtemp.

2.2.5.2 **Orgtemp** is the method template which has been created for chromatographic analytical methods. It is primarily written for organic analysis but may also be applied to such inorganic techniques as ion chromatography.

2.2.5.3 **Iorgtemp** is for most non-chromatographic methods, which comprises most inorganic analyses.

2.2.6 The template should be opened and appropriate information filled in. Most of the items which should need input are highlighted in red in the template. This does not mean that text which is black cannot be modified or even deleted if it is not pertinent to the analysis in question.

2.2.7 Draft versions of SOPs should be worked on in the "projects" drive (p: on most computers). They should then be located in the p:\sop directory under the subdirectory most relevant to the areas addressed by the SOP. For instance, in writing this SOP, it was

stored in p:\sop\qa_sops. Metals SOPs would be worked on in the p:\sop\metals subdirectory. QA will transfer the final document to the appropriate location for permanent storage and archival in order to maintain copies of all of the appropriate revisions.

2.3 Revising an SOP

2.3.1 QA will transfer the last revision of the SOP to P:\SOP\[*department*] where the author will make whatever changes are considered necessary. Note, the file will now be either a .doc file or given the extension .R00, .R01, .R02....(depending on the revision), rather than a blank template. As noted earlier, if the older version in not in the latest Word format, it should be converted. After acceptance of the revision, QA will again transfer the approved revision back to a generally inaccessible location in the QA directory.

3. Elements Of An SOP/Method

3.1 Elements

3.1.1 Almost all SOPs and methods are referred to in the general sense as SOPs. However, in some sense, they differ.

3.1.2 SOP formats are more general and free-form, not requiring the same specific elements as a Method. SOPs need only have the appropriate cover (title and revision number as on the cover of this SOP), header information, table of contents, introduction and scope, and specific operating procedures (including any appropriate appendices). Other elements may be present, depending upon the subject, but since SOPs will cover rather broad-ranging topics, no repetitive elements other than the above are currently considered necessary.

3.1.3 Methods contain the appropriate cover (title and revision number as on the cover of this SOP), header information, table of contents, introduction and scope, equipment, reagents, specific operating procedures, calibration and quality control (including corrective actions), and any appropriate appendices. They should also include data package assembly information and run sequences. Appendices should include preparation of standard solutions, a Method QC Table and a procedural flow chart.

3.1.4 All of the SOP/Method templates contain a title page. The title page consists of the following features:

- The laboratory name
- The SOP/Method number (assigned by QA Officer)
- The title of the SOP including EPA, SW846, Standard Methods or other method number reference when appropriate
- The revision history (revision number and date of approved revision)
- Signature of Author and date signed
- Signature of managerial reviewers (minimally, the QA Officer and Lab Director but may include the Divisional Manager and/or Technical Director)

3.1.5 All of the SOP/Method templates contain a header record which identifies the SOP/Method number, revision, date, page number and pages, and the method or revision it replaces (if any), such as for this SOP. The header should appear on all pages except the cover page and any pages that may be attached as appendices which are not part of the document itself. This record is not readily apparent in the "normal" mode of Word templates but must be completed by the author.

3.1.5.1 In Word, choose [View][Header/Footer]. Then fill in the appropriate information, and [Close]. This information may be modified later by following the same steps. It may also be modified by using the [Page Layout] selection from the [View] mode and changing the appropriate selection.

3.1.6 Though not required, it is preferred that the SOP also contain a footer which identifies the laboratory. It is preferred that both header and footer are separated from the document text by a double line followed (header) or prefaced (footer) by a carriage return, such as on this SOP to separate the header or footer from the text.

3.1.7 All of the SOP/Method templates contain a Table of Contents. The table of contents will be titled as such and include the header information. It should enumerate all of the major sections of the SOP and where they are located, including appendices.

3.1.8 All SOPs/Methods contain an Introduction and Scope. This section should include a brief description of the process delineated in the rest of the text. Where the process described varies from an accepted methodology (such as SW 846 or CLP), the variations should be clearly depicted in this section.

3.1.9 In methods, sample collection. storage, and holding times should be clearly outlined.

3.1.10 A part defining terms, particularly those which are specific to that procedure and may not be familiar to all readers is a valuable element of any procedure. This section is a standard part of the templates.

3.1.11 All SOPs/Methods contain a section called Equipment List and Standards (and/or reagents). All equipment and solutions necessary to complete the process described should be outlined in this section.

3.1.12 All SOPs/Methods contain a section called Safety Precautions and Waste Disposal. Any potential safety hazards should be depicted here as well as all waste disposal processes that may be entailed. If disposal involves pouring the waste into a collection container, that is all the description that is needed. The SOP then only need reference the waste disposal SOP for final disposal.

3.1.13 Where appropriate (almost always in Methods), the document should contain a section on Calibration and Quality Control. This will discuss all elements related to calibration and calibration verification. It will also discuss QC samples, frequency of all calibration and QC samples, criteria for all of these samples (including how to calculate %D, % recovery, RPD or whatever other criteria that might be appropriate), and corrective actions should any of them fail to meet their respective criteria. For most methods, a table should also be provided in one of the appendices which briefly outlines this same information. The bulk of the descriptive text, however, must appear in this section.

3.1.14 A section called Operation Procedures must be included in all SOPs/Methods which thoroughly describes the actual process. Some might consider this to be the heart of the procedure, where all analytical or other operational information is fully described in sufficient detail such that one who is reasonably familiar with the process could perform the procedure using only the SOP, with no special knowledge other than the basic principles involved and a general competence in the techniques.

3.1.15 A section should be contained in all methods called Reports. This should outline all analytical and QC reports and how they are presented, including control charts for many methods. This section should also include data package organization. If it is simpler to present some of this information in an appendix, the author may choose to use this approach. However, authors are encouraged to minimize the necessity of readers to reference too many sections of a procedure at one time to figure out all of the specifics of a process. In other words, it should be as easy to follow as possible and not force the reader to look in multiple sections of the SOP to find all of the information necessary for one relatively small part of the process.

3.1.16 Finally, SOPs and Methods, while not always required, will often contain Appendices. Two specific appendices common to most methods are a Quality Control Summary Table and a flow chart which depicts the basic steps involved in completing the process in the routine order and which includes the evaluation of successful completion of that process (i.e. "Is the QC in Control? If so, report the data. If not, what next?")

3.2 Saving the Document

3.2.1 Save the document under a name that will be readily recognizable. Generally, QA will store SOPs using the SOP number LTL-XXXX with extensions .r00, .r01, etc. to denote the revision. An update should be renamed by incrementing the extension by 1 (i.e. .r01 becomes .r02, etc.). It is not necessary that the writer of the SOP use this convention but may save it as a normal WORD .doc file with a readily recognizable name. QA will then rename the SOP when it is returned to permanent storage.

3.2.2 In Word, this may be accomplished by selecting [File][Save as] and filling in the requested information.

3.2.3 Note that if you want to save the document to any other drive or directory than it was called from, you will have to specify that path. The same conventions should be used to store the document as were discussed earlier in section 2.

3.3 After Completion of the Draft SOP

3.3.1 After the document has been written to the satisfaction of the author, it should be first passed to the department/division manager (unless that's who wrote it) for technical review. From there, the QA Officer and Lab Director will review and approve the document. QA will distribute all approved and signed documents. An unapproved (fully signed) SOP or Method document is not considered official. Other details of the document tracking process are discussed in that SOP (LTL-1002).

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1002

Title: **Document Tracking and Control**

Revision history:

Number	Date
1.0	05/15/95
2.0	12/27/95
3.0	1/06/98
4.0	12/14/99

Written by: Harry Romberg
Harry Romberg, QA Officer
Date: 12-14-99

Approved by: Kathy Kreps
Kathy Kreps, Laboratory Director
Date: 12-15-99

Controlled Document

No. 20 Assigned to: TeTra

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SOP UPDATE FORM 17

1. Introduction and Scope

1.1 Purpose

1.1.1 The purpose of this SOP is to describe the system under which Laucks creates and tracks controlled documents. This insures that the latest, approved version is in use and that prior versions are kept on file but are not available for unauthorized use. It forbids the use of unapproved or expired copies of methods or procedural documents. This includes but is not limited to procedural SOPs, QA documents, and analytical methods. Other documents may be included under this system at Laucks discretion.

1.2 Document Types

1.2.1 Laucks recognizes two types of documents.

- SOPs are considered to be administrative (such as this document or others dealing with data review or sample entry) or they may be analytical procedures (methods).
- Guidance and other miscellaneous documents may be generally broader in scope and utility than SOPs, examples being the laboratory QA Plan, Software Quality Assurance Plan or Chemical Hygiene Plan.

1.3 Scope

1.3.1 The protocol for initiating new documents is outlined, as well as the process for their approval. The tracking process is also outlined as is distribution to appropriate individuals and replacement of outdated copies with updated versions.

1.3.2 This SOP does not attempt to describe the actual creation of documents except to require that certain elements be present in order that the document may be tracked and controlled. Other SOPs (such as Elements of SOP and Method Formats) describe the structure or other elements required for a specific type of document.

2. Operation Procedures

2.1 Initiation and Updating of Documents

2.1.1 In order to track the status of documents, it is necessary to first be aware of what documents are in the process of being created, reviewed or revised. In order to do this, the Document Control Form is used (see Appendix A). Prior to beginning the creation or revision of any SOP or other controlled document, this form should be filled out. It will be kept on file in the QA Department so that it will be known which documents are in the

process of being written or revised, and who is the primary responsible person for creating, reviewing or revising it.

2.1.2 The form should be filled out by either the individual responsible for the creation or revision, their Department Supervisor, or Division Manager. Creation or revision of documents may also be assigned by the Laboratory Director, Technical Director, or QA Officer to specific individuals. The form, however, must be approved and kept on file by the QA Department.

2.1.3 Copies of this form will be given to the responsible individual and the appropriate Division Manager. Originals will be kept on file in the QA Department. This insures that all responsible parties are informed of the initiation of the creation or revision process. This form should be filled out as soon as it is determined that the creation or revision of a document is necessary and a responsible party has been assigned. These forms will also be issued approximately annually in order to initiate the review process for existing SOPs.

2.1.4 It is recognized that some documents may have been written prior to completion of the Document Control Form or that it may be decided that some documents which are already in existence should be placed into the document control system. Unless these documents are ready for immediate approval, and acceptance by the Lab Director, QA Department and/or other responsible parties, in other words, not in a draft or review status, the document control form should be filled out.

2.1.5 Shortly after the Document Control Form is approved and distributed by the QA Department, an entry will be made in a database maintained by QA which tracks the status of that document. **All documents which have been previously approved but are currently in the process of being revised will remain in force until revisions have been completed and approved.**

2.2 Tracking and Control of Existing Documents

2.2.1 Most documents, particularly SOPs and administrative documents, will be assigned document numbers beginning with LTL. The scheme for numbering documents then proceeds as follows: The most important designator is the "thousands" place. If it is unclear which "hundreds" place designator is appropriate, the one which appears to be most appropriate may be used. This SOP will not be considered to have been violated if an incorrect "thousands" or "hundreds" place designator was used but every effort will be made to use the correct designators in order to maintain a more logical organization. This organization, although preferable, is not necessary for actual control of the documents as long as each complete LTL designator is unique. Unique numbering is enforced by the SOP database.

LTL-1000	QA / Administration
LTL-2000	Health and Safety
LTL-3000	Organic Extractions
LTL-4000	Sample Control,
-4100	Project Management
-4200	Document Management and Reporting
LTL-5000	Computer Systems (LIMS / MIS)
LTL-6000	Miscellaneous
LTL-7000	Metals Digestion
-7100	ICP Analyses
-7200	ICP/MS Analyses
-7300	Graphite Furnace Analyses
-7400	Flame Atomic Absorption Analyses
-7500	Cold Vapor Atomic Absorption Analyses
-7600	Gaseous Hydride Atomic Absorption Analyses
LTL-8000	Gas Chromatography, Volatiles
-8100	Gas Chromatography, Semivolatiles
-8200	GC / Mass Spectrometry
-8300	HPLC
-8400	Other Organic Analyses
LTL-9000	Conventional Chemistry- Titrimetric Analyses
-9100	Conventional Chemistry- Spectrophotometric / Instrumental Analyses
-9200	Conventional Chemistry- Gravimetric Analyses

2.2.2 Original documents will always be given a revision number of 0. Subsequent revisions, no matter how minor the revision, will be incremented by one.

2.2.3 In addition to the numbering and revision documentation, the document must also be given a title which will uniquely identify the document content. If the document is an analytical method, the method reference should be incorporated into the title. One example of this might be "Organochlorine Pesticides and PCBs by SW 846 Method 8081A."

2.2.4 SOPs, Methods, and many other documents must have header information which clearly indicates the document number, revision, date of revision, and document replaced by

revision. Page numbers and the total number of pages in the document are strongly recommended and usually required, although some discretion may be allowed by QA in special circumstances. The header may vary in format but must contain all required information similar to the following. SOPs which have been created using the template described in the Laucks SOP on the Elements of SOP and Method Formats will contain the header information as described.

SOP No: LTL-xxxx
Revision: 1
Date: 12/14/99
Page: x of xx
Replaces: 0

2.2.5 As a minimum, approved documents are signed by the author, QA, and the Laboratory Director. They may also be signed by other critical supervisory personnel as deemed appropriate by QA. In general, methods will either be written by these supervisory personnel and not require an additional signature, or they will be written by an individual (signed), reviewed by a supervisor (signed), and approved by QA and the Lab Director.

2.2.6 Once a document has successfully undergone review and been signed-off by the author of the document and all of the other appropriate individuals (Laboratory Director, QA Officer, and, where appropriate, Technical Director, Division Managers, etc.), it is added to the SOP database list. Only approved documents and their most currently approved revisions are noted on these lists. These lists are broken down by department and distributed to department supervisors with the distribution date indicated. New lists are distributed whenever a new document or revision is added.

2.2.7 A database is maintained by the QA Department which, as a minimum, will track the document number, Department, revision number (or New or Draft if the document is incomplete), responsible individual, title and SOP Manual distribution (if the document has been completed and approved). Also tracked are the most recent revision date, the next revision due date, the last review date and, if any version existed under the previous SOP system, the previous SOP number. Only the applicable fields among these latter fields need be filled out. A copy of the screen form is presented in Appendix B.

2.2.8 Types of reports available from the SOP database include a table of contents for each SOP book, which are printed out whenever SOPs are released, automated Document Control Forms similar in content to the one in Appendix A, reports on SOPs due for review, and reports on SOPs overdue for review. The latter forms enable QA to assign and to track the status of SOPs which are up for their annual review. As this is an Access

Database, any other type of query or report form can be generated that uses any of the information previously noted in the above paragraph and in Appendix B.

2.2.9 Copies of the most current documents are kept on file in the QA Department and departmental specific documents are kept by the departmental supervisor in ring-binders which are available to all analysts and other appropriate staff. The SOP manuals are maintained in key locations throughout the laboratory. The SOP manuals contain only those SOPs pertinent to that area of the laboratory. The SOP manual locations are presented in Appendix C. These departmental copies are stamped with a Controlled Document Stamp (See Appendix D) in either red or black annotated with red pen. These copies, which are tracked by the QA department, will be replaced when a newer version has been completed and signed-off. The color of the Controlled Document Stamp and/or annotation, will be black on subsequent secondary copies and will not be directly tracked by the QA department as these documents are considered uncontrolled.

2.2.10 It is the **Departmental Supervisor's** responsibility to ensure that their staff have copies of the most recent version of any document available to them. Keeping copies of outdated versions is inappropriate as they may be inadvertently used by uninformed individuals. When revised versions are issued, the old versions will be collected from the SOP books and usually disposed. In addition, the SOP book table of contents will be updated to reflect the revised SOP(s).

2.2.11 It is inappropriate for any individual to be working from an unapproved copy of a method or procedure. This means that individuals must not be working from copies of controlled documents. If an individual must consult an SOP, they must consult a controlled copy, which is readily available in a number of areas throughout the laboratory.

2.2.12 When documents are distributed to the departmental supervisor, a copy of the signature list(s) for the specific document(s) is/are also distributed. The signature lists are returned to the QA department when completed.

2.2.13 Departmental supervisors will ensure that the most recent versions of all appropriate documents are made available to all affected staff members. When this occurs, three things must happen.

- Newly distributed versions are placed in the SOP manuals.
- The signature lists for the current documents are signed and dated as staff complete reading the SOPs. In addition, as staff new to a particular task (SOP) are trained, the departmental supervisor will ensure that they have read and signed the signature list

for that SOP. This may require that the supervisor request a new SOP signature list for that staff member so that they can sign the SOP for newly assigned tasks.

- The departmental supervisor is responsible for ensuring that all outdated versions of SOPs are discarded or destroyed when the newer revisions are issued.

2.2.14 Note that although any person capable of performing a documented task should be in possession of or have access to a current, officially assigned copy, the possession of a copy of any SOP or method does not imply that the individual in possession is qualified to perform the task detailed. They must still be properly trained in the techniques involved.

2.2.15 Note that versions of methods or SOPs which have been given to regulatory agencies or clients are generally uncontrolled in that they will not be updated except by specific arrangement. Controlled documents may be released to clients upon specific arrangement. However, the laboratory can only control the document and any updates up to the point they are provided to the client. It becomes the client's responsibility to then ensure that they are referencing the most recent versions in their own documentation.

2.3 Storage and Filing of Controlled Documents

2.3.1 Controlled documents will be kept by the QA Department. Master originals of the documents will be stored in a secure file and will generally not be used except to act as the reference copy and make intermediate "reproduction" copies.

2.3.2 Reproduction copies will be used to make subsequent copies for distribution to the laboratory and other authorities. These will be filed in QA but may not be stored in the same secure manner as the master copies.

2.3.3 Both master original and reproduction copies will be filed in order of their SOP number as defined previously.

2.3.4 Electronic versions of all controlled documents are also kept on file by QA. These versions are stored in an area of the laboratory network which has limited access to designated individuals. These electronic copies will be given names as closely matched as possible to their document or SOP number. Original documents and revisions will be given the extension .R00 or .R01, etc. to indicate their revision number. Should multiple files be necessary to create a given document, they will be incorporated into a subdirectory with similar naming conventions.

2.3.5 Copies of these electronic versions of SOPs will be distributed to individuals who have been assigned a revision. No other copies of these controlled documents should be kept by laboratory staff in order that unapproved copies of the document do not proliferate.

2.4 Review and Updating of Documents

2.4.1 In order to facilitate updates to documents without violating the practices outlined in the SOP, and in order to insure all approved updates have indeed been incorporated into the document, an "SOP Update" form (Appendix E) should be used. This form may be filled out at any time by an analyst or supervisor. Before the change can be brought into practice, however, it must approved by QA. QA may also choose to consult the area supervisor, Division Manager, or other senior staff before incorporating the procedure into the routine practice. A copy of this form will be kept with the laboratory controlled copy **AND** a copy must be filed with QA. When it is time to update the SOP, changes outlined on these forms will be incorporated into the revision.

2.4.2 Unless major changes to SOPs are required, SOPs should be reviewed approximately annually. Changes which do not require immediate update are typos or wording changes which do not inhibit the correct interpretation of the operation involved. Items which could lead to misinterpretation or incorrect performance of the methods should be corrected as soon as feasible. At the time of any revision, items addressed in the "SOP Update" forms will be incorporated into the SOP. In addition, any other updates determined at the time of the review will be added. Each review will be documented on the Document Control Form (Appendix A).

Appendix A

Document Control Form

Laucks Testing Laboratories

DOCUMENT CONTROL FORM

_____ Generate new document

_____ Modify existing document

_____ Review existing document

Document No.: _____

Document Title: _____

_____

_____

Assigned to: _____ Date: _____

The aforementioned document has been reviewed and does not require modification at this time:

Reviewer: _____ Date: _____

Purpose for generation or modification of document and comments on review:

_____

_____

_____

_____

_____

_____

QA Approval: _____ Date _____

Appendix B

SOP Database Screen

Use the [Page Up] and [Page Down] keys to browse through the Document List

Search for a record | Go to top of DOC. List | Open a blank record | Update Assignment List | Delete this record | Close Doc. List Window

Current Document #: LTL-1002
Revision Date: 12/27/95
CHOOSE Department: Quality Assurance
Next Revision Due: 7/15/96
Revision #: 002
Last Review Date: 12/27/95
CHOOSE Supervisor Name: Romberg, Harry .
Previous Document #: LTL-0054
Document Name: Document Tracking and Control.

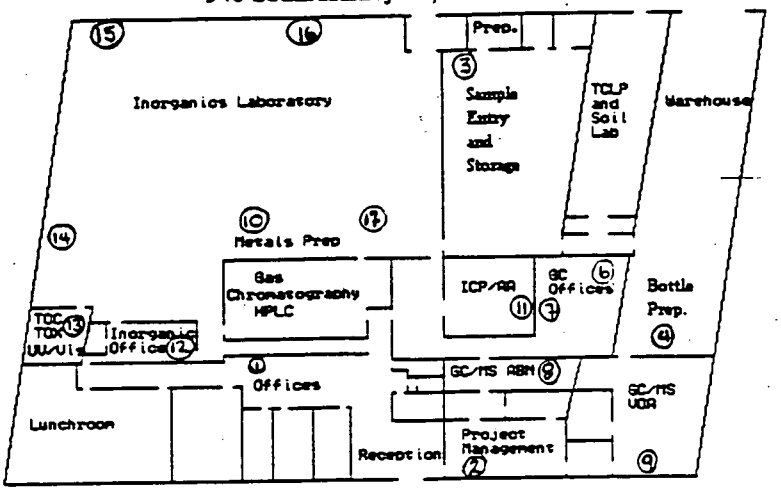
Department Abbreviation: QA
Current SOP #: LTL-1002
SOP Distribute: Yes

Record: 1 of 13

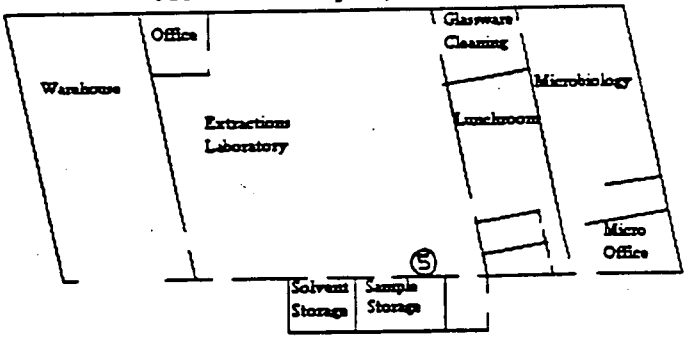
Appendix C

SOP Manual Distribution Locations

Laucks Testing Laboratories, Inc.
940 South Harney St., Seattle



Laucks Testing Laboratories, Inc.
921 South Harney St., Seattle



SOP Book Location

Appendix D

Document Control Stamp

Controlled Document

No. _____ Assigned to: _____

Appendix E

SOP Update Form

Laucks Testing Laboratories

SOP UPDATE FORM

Document No.: _____

Document Title: _____

_____

_____

The following changes have been reviewed and determined to be necessary to the implementation of the above document.

_____

_____

_____

_____

_____

_____

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_____

Submitted by: _____ Date: _____

Approved by (QA): _____ Date: _____

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1003

Title: Chain-of-Custody and Documentation Procedures

Revision history:

Number	Date
1.	2/13/95
2	2/3/98

Written by: Harry Romberg Date: 2-3-98
Harry Romberg, Quality Assurance Officer

Approved by: Karen J. Kotz Date: 2/3/98
Karen Kotz, Laboratory Director

UNCONTROLLED

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1. Introduction and Scope

1.1 Description

1.1.1 This SOP is intended to describe the chain-of-custody process at Laucks, for all samples from the point of receipt until the time of sample disposal. It does not address actual sample receipt, entry and log-in, nor does it address any aspect of samples analysis or reporting of results except as it pertains to maintaining the chain-of-custody. The chain-of-custody process is described only for samples requiring secure storage and strict chain-of-custody documentation.

1.1.2 The location of all samples requiring secure storage must be known at all times over the course of their possession by Laucks. Failure to maintain these conditions may result in invalidation of data on legal grounds, regardless of the technical level of data quality.

1.1.3 This process is restricted to use by, or under the supervision of analysts experienced in the process described. Each analyst or other individual requiring possession of the samples for any reason must understand the necessity of this documentation chain and be familiar with the process. Any person requiring access to the samples outside of the secure storage area must check them out using the described procedures.

1.1.4 Virtually all analytical staff and many others employed by Laucks are considered authorized personnel and may have access to one or more of the secure storage areas as needed for performance of their duties, at the discretion of the individual, and depending upon the nature of their duties. Removing of the samples or any aliquots thereof from the secure areas, however, requires completing the forms provided for this purpose. Individuals who are not Laucks employees will not have access to samples except under the direct observation and accompaniment of staff members.

1.2 Definition of Terms

1.2.1 Custody - A sample is considered under custody if:

- It is in the possession of an authorized person
- It is in view after being in the possession of an authorized individual
- It was in the possession of an authorized individual who then locked it up
- It is in a designated secure area which is accessible only to authorized personnel.

1.2.2 Chain of Custody - The process by which custody of a sample is maintained and documented throughout the period that the sample is in the possession of the laboratory.

Any changes in the possession (custody) of the sample must be documented in order that the chain-of-custody can be properly maintained.

2. Equipment List

- Secure Storage Custody Log(s), see Appendix A
- Volatiles Custody Log(s), see Appendix B

3. Safety Precautions

3.1 Safety Precautions

3.1.1 No safety precautions are necessary for adherence to the items addressed by this SOP. However, in handling actual samples while operating under this document, all standards, samples and sample solutions should be handled as if they are hazardous substances.

4. Operation procedures

4.1 Identification of Samples Requiring Strict Chain-Of-Custody

4.1.1 Almost all samples entering the laboratory come with chain-of-custody logs, either generated by the client or by Laucks. Often these chains-of-custody are intended only for clear identification of testing parameters, rather than actual custody maintenance. These custody logs, however, will always be signed, timed and dated by the person checking the samples in and entering them into the laboratory database.

4.1.2 Actual internal chain-of-custody procedures will be followed for all project and other work which require such procedures. These are usually identified as CLP work or work which require similar deliverables. These samples will usually, although not always, arrive with custody seals on the coolers and sometimes even the sample containers themselves. All work under the HAZWRAP, NFESC, or Army Corps of Engineers require these procedures, regardless of the type of deliverables requirements, as does any work involving pending legal action. If it is uncertain whether or not strict chain-of-custody should be maintained, these procedures should be followed.

4.2 Initiating Internal Chain-Of-Custody

4.2.1 Internal chain-of custody procedures begin when the samples are logged into the laboratory database. When the samples are logged into the system, they are stored in or near the sample entry area, in the main laboratory, in one of 3 locations:

- The main walk-in cooler is for organic extractables which have not yet been transferred to the extractions laboratory and for inorganics which require refrigeration.
- The volatiles refrigerators are located in the area between the GC room and the laboratory computer system hub.
- The locked "cage" in the log-in area is for samples not requiring refrigeration.

4.2.2 Additionally, samples requiring secure storage which are located in the walk-in will be on designated shelves. Those awaiting transferal to the organics extractions laboratory will be on their own designated shelf.

4.2.3 All of these areas are secured under lock and key, the keys being in the possession of sample control and, in the case of the volatiles refrigerators, in the possession of key analysts in those areas.

4.2.4 Samples requiring secure storage are logged into any of these areas by the sample receiving representative using a Secure Storage Custody Log (Appendix A). Samples not requiring secure storage need not have this form completed. A custody log will be completed for each **workorder** for which samples require chain-of-custody procedures.

4.3 Maintaining Internal Chain-Of-Custody

4.3.1 When samples are logged out of storage areas, they will be signed out in the appropriate spaces by the person removing them.

- If they are being removed for analysis, the "**Action**" column should state the analyses being performed. When they are returned, the logsheet must also indicate such. Additionally, the "**Sample Numbers**" column should indicate which samples are being removed for analysis (i.e. 1-10 metals digestion, or 3-5 NO3/NO2 analysis).
- If they are being removed for transferal to another location (i.e. extractions), the "**Action**" column should state where they are being transferred. Additionally, the "**Sample Numbers**" column should indicate which samples are being transferred (i.e. 1-10 volatiles, or 3-5 extractables).
- When samples are removed for final disposal, if all samples are being removed, the logsheet is signed and dated at the bottom of the page. If only certain samples are being disposed or to be even more clear, the "**Action**" column should indicate "disposed" and the "**Sample Numbers**" column should indicate which samples are being disposed.

4.3.2 When samples are signed into another storage location, this is done using an identical Secure Storage Custody Log. Samples which are subsequently removed from these areas for analysis or disposal should be signed out using the same procedures as above.

4.3.3 Volatiles samples, being generally for a single analysis, are signed out using an abbreviated logsheet. Copies of GC/MS and GC VOA logsheets are located in Appendix B.

4.3.4 Any analyst removing samples from **any** secure storage area for the purpose of preparation or analysis or transferal to another department **must** sign the samples out using the Secure Storage Custody Log and must sign the samples back in when they are returned, or must sign them into another secure storage area. Samples must be in the possession of the analyst who signed them out at all times during this period and must not be left unattended. If samples are analyzed and then immediately disposed, as may be the case for some volatiles analyses, the "**Action**" column on the custody log should indicate "analysis and disposal." Note, in checking volatiles samples out using a volatiles custody log, it is assumed that the purpose is to analyze for volatiles since no other analysis is performed on these samples.

4.3.5 There is ample room on any one Secure Storage Custody Log in almost all cases to accommodate checking all sample containers for a particular SDG or workorder in and out as often as required for all of the pertinent analyses from that secure area. Should an additional page be required, it should be obtained from Sample Entry. A second (or third) page must not be initiated until all of the space on the previous form has been filled. The first page must be marked "1 of 2" in the upper right corner and the second page marked "2 of 2". In the unlikely event that even more pages are required, this mark can be crossed out (single line, initialed and dated) and the sheets marked "1, 2, or 3 of 3, etc.

4.4 Sample Disposal and Closing of the Internal Chain-Of-Custody

4.4.1 When samples have been signed out for final disposal the chain-of-custody process is considered to be complete. The Secure Storage Custody Logs must be collated, bound and turned in to the Quality Assurance Department in order that the chain-of-custody can be tracked for all samples requiring this process, should such tracking be required at a later date.

4.5 Review of Custody Logs

4.5.1 On at least a quarterly basis, supervisory personnel must review selected custody logs to insure they are being filled out properly and completely. The supervisor need not review

all of the forms but must review at least 5% or 10 forms, whichever is greater. The supervisor will stamp the reviewed forms with a "reviewed by" stamp , initialing and dating the notation or may write "reviewed by" by hand, likewise initialing and dating the form. The supervisor should also cursorily review the remaining forms to make sure there are no blatantly obvious omissions but need not mark these forms unless a discrepancy is observed.

4.5.2 Review should include noting that all spaces are filled in properly and completely (this especially means that all samples that were checked out must be checked back in and that the person handling the samples must be identified), that errors are crossed out with a single line, initialed and dated, that entries are clear and not obliterated.

4.5.3 Should the supervisor find errors or omissions, the must issue a corrective action form to the individual who made the error (if it is obvious who that is) or to the appropriate supervisor. Any of these individuals can correct the form (initialing and dating the correction). The primary purpose of the corrective action notice is so that the individual in error be re-trained as to the proper custody procedure.

4.5.4 Supervisors responsible for this review may assign the responsibility to other capable individuals but the ultimate responsibility is theirs. These supervisors are the Organics Division Manager for the volatiles logsheets, the Extractions supervisor for the extractables, and the Sample Control supervisor for the main lab walk-in and unrefrigerated secure storage areas.

Appendix A

Secure Storage Custody Log

Laucks Testing Laboratories, Inc.

Secure Storage Custody Log

Project:_____ **LTL Number:**_____

Number of Containers (*optional*)**:**_____

Storage Unit:_____ **SDG Number** (*optional*)**:**_____

Sample Number	Matrix (*optional*)	Location (*shelf*)	Logged Out			Logged In			Action
			Date	Time	By	Date	Time	By	

Samples Disposed of by _____ on _____

Appendix B

Volatiles Custody Logs

LAUCKS TESTING LABORATORIES
GC/MS VOA CUSTODY LOG

LABORATORY NUMBER	SAMPLE NUMBER	DATE & TIME REMOVED	BY	DATE & TIME RETURNED	BY	COMMENTS

GC Volatiles Custody Log
Laucks Testing Laboratories, Seattle, Washington

Samples	Analysis	Date/Time Removed	Analyst	Date/Time Returned	Analyst	Comment

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1004

Title: **Documentation of Analyst Competence and Training**

Revision history:

Number	Date
1.0	01/31/95
2.0	12/27/95
3	6/23/96
4	8/4/99

Revised by: Harry Romberg Date: 8-4-99
Harry Romberg, Quality Assurance Officer

Approved by: Kathy Kreps Date: 8-4-99
Kathy Kreps, Laboratory Director

Controlled Document
No. 20 Assigned to: Tetra

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1. Introduction and Scope

1.1 Description

1.1.1 This SOP describes the way in which analyst competence is initially documented and by which the analyst is considered capable to perform independent analysis. Two practices are in place at the time of this writing. One practice is designed primarily for analysts who have been employed doing an analysis for a significant period of time at Laucks and have demonstrated competence through the successful analysis of many samples, including one or more of the following: performance evaluation (PE) samples, reference materials, laboratory control samples, surrogates, etc. The other practice is primarily for analysts who have been performing a specific analysis for less time than is considered extended proof of competence. This practice involves the analysis of multiple aliquots of a PE sample and subsequent evaluation of the results. *This practice also usually includes the completion of training checklists for the task for which the analyst is being trained.*

1.2 Scope

1.2.1 This SOP contains discussion of initial demonstration of competence through PE analysis and, for some analyses, P&A criteria. It also defines ongoing performance demonstration through the use of PE samples.

1.2.2 Specific elements of training in safety, QA, and in each department are maintained in separate files. However, quizzes and sign-off sheets from this training are included in the respective analyst's file as demonstration that such training occurred. Specifics of these types of training are not within the scope of this SOP.

2. Definitions

- **PE** - Performance Evaluation
- **P&A** - Precision and Accuracy
- **Trainer** - An individual who has documentation demonstrating experience recognition or successful completion of competency and has been performing the task/method for a minimum of 3 months experience for login, sample preparation, and reporting and a minimum of 6 months for analytical instrumentation operation and analysis reporting.

3. Responsibilities

3.1 Analyst

3.1.1 It is the responsibility of the analyst to complete all of the items of their required training in an appropriate timeframe as required by their manager, safety and QA.

3.1.2 The analyst must complete all demonstration of competency items outlined in this SOP in a manner consistent with the analytical SOP.

3.1.3 The analyst must analyze a PE study initially and on an ongoing basis (at least annually) for each method for which they are considered qualified.

3.1.4 For many analyses, the analyst must perform an initial Precision and Accuracy study as required.

3.1.5 The analyst must regularly perform all required method QC, including matrix and blank spikes and laboratory control sample analyses, which may be used to qualify them for competency.

3.2 Supervisor

3.2.1 It is the supervisor's responsibility to ensure that their analysts are all initially qualified to perform an analysis including ensuring that they have analyzed all required PE samples and performed all required P&A studies for the methods for which they will be doing analyses.

3.2.2 It is the supervisors responsibility to ensure that all analysts have participated in applicable QA and safety training.

3.2.3 It is the supervisor's s responsibility to ensure that on a continuing basis, at least annually, that analysts who are to be considered capable of performing an analysis, have performed within limits on at least one PE study for analyses for which such are available.

3.2.4 It is the supervisor's responsibility to ensure that other training has occurred, whether that means peer training, reading, quizzes, completed checklists, etc.

3.2.5 It is the supervisor's responsibility to develop and maintain current departmental training materials, such as checklists, quizzes, etc.

3.2.6 It is the supervisor's responsibility to ensure that the analyst's training file has been updated with the most current PE or P&A data as well as any quizzes or checklists that are considered part of their departmental training.

3.2.7 It is the supervisors responsibility to designate a qualified individual(s) to train personnel for their new task/assignment.

3.3 QA

3.3.1 QA maintains training files (except for Extractions where the supervisor maintains the files due to the location of the extractions facility).

3.3.2 QA periodically audits training files to ensure appropriate training is being maintained.

3.3.3 QA reviews PE and P&A studies to ensure criteria have been met.

3.3.4 QA works with managers to assist in developing training materials.

3.3.5 QA provides training to staff in QA issues and ensures that documentation of this training is in the staff training file.

3.4 Trainer

3.4.1 Completes applicable staff training documents during the training process.

3.4.2 Reviews documentation with the individual and the supervisor to ensure timely and accurate review of progress and documentation.

4. Operation procedures

4.1 Recognition of Experience and Training

4.1.1 Many analysts have been performing their assigned duties for an extended period of time and have successfully analyzed many samples, reference materials, PE samples, matrix, blank, and surrogate spikes and have not only demonstrated their capabilities to achieve results which meet criteria but have demonstrated a thorough knowledge of all aspects of the chemistry involved, instrument performance and maintenance, the necessary data reduction requirements, quality control criteria, and documentation.

4.1.2 These analysts, at the discretion of the appropriate Division Manger, may be certified to independently perform their analytical duties. This is achieved using the Recognition of Experience and Training Form, an example of which is in Appendix A. This form contains space to note the analysis type (Cyanide, for example) and the methods by which

they are considered competent (335.3 and 9012 perhaps, but not CLP). The dates from which they have been doing these analyses must also be noted on the form. The Division Manager then signs the form in order to certify that the analyst is considered adequately trained in the particular method or aspect of the job. The form must include the criteria used to designate someone as competent and attached to the form must be the applicable documentation to confirm the criteria have been met.

4.1.3 Certification of competency must include the successful analysis of a performance evaluation (PE) sample where such are available or can be made in the laboratory by a supervisor. This sample will be blind to the analyst, must be analyzed independently by them and must be analyzed in accordance with the appropriate SOP. Greater specifics on these types of samples are given in the Laucks SOP entitled "Blind Spike Program" but will often be from a WP or WS study or from another commercial source. Analysts who have been performing analyses for any length of time at Laucks have almost certainly analyzed numerous PE samples which can be used for initial and ongoing demonstration of competency.

4.1.3.1 Adequate performance on a PE sample will be considered to be within the supplied statistical limits for that sample if from a commercial source or from method defined limits for an LCS or blank spike if from internally prepared material.

4.1.4 Precision and Accuracy (P&A) criteria using quadruplicate analysis are also a part of most organic SW846 and some other methods. Successful analysis of such samples will be considered to be within the reference method-specified criteria. Since Laucks own precision and accuracy limits must be within the method-specified criteria, the analyst should also be able to meet Laucks criteria as well as those of the reference method. However, as long as method criteria are met, the analyst may be approved for independent work as long as they are able to obtain satisfactory performance from the ongoing analytical QC for that analysis.

4.1.5 Competency may also be demonstrated by successful analyses of any combination of at least 3 each of at least two types of spiked QC samples (blank spikes, matrix spikes or lab control samples). These may be documented on the forms in Appendix B and the training forms in Appendix C but a summary must accompany the certifying form which either includes or provides reference to the data.

4.1.6 It is acceptable to certify such capabilities on multiple forms and to certify for multiple analysis types and/or methods on one form. At the time of this writing, there may be no known materials which can be submitted as unknowns for some analyses. In this event, at the discretion of the Division Manager and Quality Assurance Officer, this form may also be used to qualify analysts. From the date of the first version of this SOP, however, this should not be done where materials are readily available and reasonably handled.

4.1.7 When this process is completed, the original of this form and a copy of all applicable documentation will be inserted into the analyst's training file which is maintained in the QA area for the 940 building and the Extractions Supervisor Office for the 921 building.

4.2 Demonstration of Capability to Perform Analysis

4.2.1 For analysts who are relatively new to their assigned tasks, a greater degree of capability demonstration must be undertaken through the satisfactory completion of any internal departmental training documentation. This training will include specific training and documentation developed by that department and department manager and may include required reading, quizzes, and performance criteria at the discretion of the department manager and QA. Example checklists are provided as Appendix C.

4.2.2 In general, if an analyst has not passed the criteria detailed in 4.1, then he/she must proceed through the following:

4.2.2.1 A trainer is designated for the task/test

4.2.2.2 One-on-one training occurs for the timeframe designated by the supervisor and applicable checklists.

4.2.2.3 Training may also include required reading of SOPs and the QA Plan, quizzes, and subset task demonstrations.

4.2.2.4 Progress is monitored and documented on applicable forms.

4.2.2.5 Supervised training continues until the analyst is deemed ready for capability demonstration.

4.2.2.6 Demonstration of analytical competency completion, however, will be the same. Performance Evaluation and/or P&A elements as described previously in 4.1.3, 4.1.4 *or 4.1.5.*

4.2.3 Where P&A demonstration is not required and defined by the method, Laucks may choose to apply additional internal P&A criteria similar to a typical P&A study. The samples may be submitted by the QC Officer, the Division Manager, or an individual designated by one of the above. Four or more aliquots of a material will be submitted to the analyst as unknowns. The analyst must demonstrate the capability to achieve results within the recovery range specified by the manufacturer, if they are independent materials, or within laboratory recovery criteria if they are prepared in-house. In addition, the % RSD of the results must be within Laucks established RPD limits (or default RPDs if none exist for a specific target analyte).

4.2.4 It is recognized that some independent materials may not recover within manufacturers criteria, at least for a subset of the target analyte list, regardless of the experience and competence of the analyst, due to degradation of the material, arbitrary setting of the limits, determination of the "true" values by methods other than those used for the analysis, or other factors. In that case, the % RSD may be the major factor in evaluation and other considerations or action may be taken at the discretion of the QC Officer and/or Division Manager, such as how Laucks more experienced analysts have historically performed for a particular material.

4.2.5 Failure to meet criteria means that the analyst must continue to work under the close supervision of a trained analyst.

4.2.6 Likewise, meeting these criteria may be determined to be only one step in the overall training process. Whereas this is demonstration that the analyst is capable of obtaining reliable results, the Division Manager or other supervisory personnel may determine that a more complete knowledge of the analytical process is in order, such as instrument maintenance capabilities, method troubleshooting, data reduction, proven performance on actual sample analysis, etc.

4.2.7 When such materials are analyzed, a Demonstration of Capability to Perform Analysis form is completed (see Appendix B). This form is designed for single analyte methods. For multi-analyte materials, a page may be attached which depicts all of the analyst's results and the control criteria. However, this is the final signature form and must accompany any summary pages or written evaluation which may be considered pertinent. Also attached should be copies of the supporting data or a data summary page which references the workorder under which the data may be found.

4.2.8 The date of analysis, the results, the recoveries, and the % RSD are recorded on the form (or the attached summary). If all analytes met or did not meet criteria, the appropriate box is checked. If not all criteria are met but the analyst was considered to have performed adequately, a narrative explanation must accompany the evaluation, either on the back of the form or as a separate, attached report.

4.2.9 Additionally, if the analyst, through the analysis of these samples is considered fully qualified to perform the analysis, the appropriate box is checked and the form signed by the Division Manager. If the Division Manager considers that the analyst is now capable of analysis but still requires additional experience and training before they are fully capable of independent analysis, a date is set to review performance. The additional experience or training required and the next performance review date are recorded on the form (with the appropriate box checked) and initialed.

4.2.10 *Alternatively, training checklists for many tasks have been developed. In the case of analytical duties, these may include reference to the completion of P&A or PE studies or individual QC analyses as previously discussed. Completion of one of these training checklists (including appropriate signatures) is considered demonstration of training. However, PE or P&A results or other appropriate documentation should also accompany the training checklist as demonstration of competency.*

4.2.11 If further training is still required, copies of these forms will be retained by QA in a file to be reviewed regularly to insure that this final analyst review occurs in a timely fashion. A copy of the form indicating interim status will also be retained in the staff member's training file.

4.2.12 When this process is completed, the original of this form will be inserted into the analyst's training files.

4.3 Ongoing Demonstration of Performance

4.3.1 At least annually, after initial qualification, analyst proficiency must be demonstrated. Each staff member that performs a method must demonstrate their continued proficiency through analysis of single blind proficiency samples (another PE). WP, WS or commercial PE samples may be used to satisfy this requirement just as they were used for initial qualification.

4.3.2 As with initial qualification, continuing performance must be documented in the analyst's training file. Ongoing competency can be documented using the Recognition of Experience and Training Form.

5. References

Navy Installation Restoration Laboratory Quality Assurance Guide, Naval Facilities Engineering Service Center, February 1996

Laucks SOP

LTL-1011 Procedures for the Determination and Reporting of Detection Limits, Reporting Limits, Precision and Accuracy Studies, and Control Limits

Appendix A

Recognition of Experience and Training Form

Recognition of Experience & Training Form

Laucks Testing Laboratories

It is hereby recognized that _____

Employee Name

has demonstrated competence in the methodologies listed below. Through the successful analysis of numerous samples, including performance evaluation samples, matrix spikes, laboratory control samples, etc. and in the associated reduction of data as required by these methods, we certify this staff member as being capable of independent performance of the listed analyses.

Analysis Type	Method Numbers	Has Been Performing Analyses by These Methods Since	Has Demonstrated Competency by meeting the following criteria, with the hard copy of applicable information relating to this competency attached to this form

_____ Division Manager

_____ Date

Appendix B

Demonstration of Capability to Perform Analysis Form

Demonstration of Capability to Perform Analysis

Laucks Testing Laboratories

Analyst:_____

The above analyst has independently analyzed at least 4 aliquots of the listed performance evaluation material, which were submitted as blind samples, achieving the listed recoveries. The limits specified by the manufacturer are considered within acceptable range or, if prepared by Laucks from known materials, the laboratory established control limits apply. In addition, the % relative standard deviation (%RSD) of these data is evaluated against the laboratory established RPD limits as set at the time of this evaluation.

Method:_____ PE Material:_____

Target Value:_____ Recovery Criteria:_____

Reproducibility Criterion:_____

Date	Result	% Recovery
%RSD		

Criteria for non-analytical functions:_____
Demonstrated by:_____

Met Criteria Did Not Meet Criteria

These data are considered adequate demonstration of independent performance if all criteria are met. Other factors may prevail, at the discretion of the appropriate Division Manager before any analyst may be allowed to independently analyze actual samples.

Analyst has met performance criteria but requires more experience. Specific areas which require further training or experience are _____
Work will be reviewed in _____ and capabilities evaluated. *[Initial here. Do not sign below]*

Analyst has met performance criteria and has been found fully capable of independent work. *[Sign Below]*

_____ _____
Division Manager Date

compdemo.doc/rev.2 12/13/95

Appendix C

Example Training Checklists

Laucks Testing Labs
Pesticide/Herbicide GC Semivolatile Analyst Training Verification Checklist

Analyst Name:		Date:	Trainer:	Supervisor:	Analyst:
Documentation					
1	Able to use Standards Log				
2	Able to use Instrument Run Logs				
3	Able to use Instrument Maintenance Logs				
Methods					
4	Has read and understands SOPs for all applicable methods				
	List Method(s): _____				
5	Has read and understands EPA Methods (SW846, CLP, 500 & 600 series)				
	List Method(s): _____				
6	Has read and understands appropriate sections of GC Training Manual				
Instrument Operation/Maintenance					
7	Knows location and use of Instrument Manuals				
8	Knows basic GC theory				
9	Able to use GC Control Pad to set temperature program				
10	Able to use Autosampler Control Pad to set injection program				
11	Able to change syringe, septa & injection port liner				
12	Able to trim/change columns, install Y connector & perform leak check				
13	Able to measure and set carrier and makeup gas flows				
14	Able to bake column/injectors/detectors				
15	**NON-ROUTINE:** *Able to change detectors*				
16	**NON-ROUTINE:** *Able to perform total system cleaning*				
Analytical Performance					
17	Able to prepare standards & pass standard QC acceptance criteria				
18	Able to analyze breakdown check and apply QC acceptance criteria				
19	Able to analyze and generate acceptable calibration curve				
20	Able to analyze CCVs and apply QC acceptance criteria				
21	Applies acceptance criteria for surrogates and spikes				
22	Able to set up analytical runs (CLP & non-CLP) & acquire data				
23	Able to get information on samples/analyses (test codes, MDLs, etc.)				
24	Able to quantitate an analytical batch (standards, CCVs, QC & samples)				
25	Knows how to confirm detection of analytes (peak ID, conf. col.)				
26	Knows reanalysis and reextraction criteria				
27	Able to perform sample dilutions (obtaining linear results)				
28	Knows correct reporting limits for method(s)				
29	Knows corrective action & documentation for out of control QC events				
30	Able to produce a data package (In-house, CLP and SW-846)				
Method Validation *(complete one or more of the following)*					
31	Has successfully analyzed four P&A samples				
32	Has successfully analyzed two PE samples				
33	Has successfully analyzed three each of two types of QC samples				

This is to certify that _____ has been an analyst in the GC semivolatile department and has demonstrated competency at the preceeding tasks for the following methods (list below):

_____

Items found to be not satisfactory at the 3 month interval should be discussed with the analyst and further training done. Not satisfactory items should be re-evaluated at the end of the 6 month probationary period.

Laucks Testing Labs
GC Volatile Analyst Training Verification Checklist

Analyst Name:		Date:	Trainer:	Supervisor:	Analyst:
Documentation					
1	Able to use Standards Log				
2	Able to use Instrument Run Logs				
3	Able to use Instrument Maintenance Logs				
Methods					
4	Has read and understands SOPs for all applicable methods				
	*List Method(s):*_____				
5	Has read and understands EPA Methods				
	*List Method(s):*_____				
6	Has read and understands appropriate sections of GC Training Manual				
Instrument Operation/Maintenance					
7	Knows location and use of Instrument Manuals				
8	Knows basic GC theory				
9	Able to use GC Control Pad to set temperature program				
10	Able to use Autosampler Control Pad to set injection program				
11	Able to check system flows				
12	Able to trim/change columns & perform leak check				
13	Able to measure and set carrier and makeup gas flows				
14	Able to bake column/injectors/detectors				
15	**NON-ROUTINE:** *Able to clean P&T and autosampler lines*				
16	**NON-ROUTINE:** *Able to change nickel tubing, resin and IPA*				
Analytical Performance					
17	Able to prepare standards & pass standard QC acceptance criteria				
18	Able to analyze and generate acceptable calibration curve				
19	Able to analyze CCVs and apply QC acceptance criteria				
20	Applies acceptance criteria for surrogates and spikes				
21	Able to set up analytical runs & acquire data				
22	Able to get information on samples/analyses (test codes, MDLs, etc.)				
23	Able to quantitate an analytical batch (standards, CCVs, QC & samples)				
24	Knows how to confirm detection of analytes (peak ID, conf. col.)				
25	Knows reanalysis criteria				
26	Able to perform sample dilutions (obtaining linear results)				
27	Knows correct reporting limits for method(s)				
28	Knows corrective action & documentation for out of control QC events				
29	Able to produce a data package (In-house and SW-846)				
Method Validation *(complete one or more of the following)*					
30	Has successfully analyzed four P&A samples				
31	Has successfully analyzed two PE samples				
32	Has successfully analyzed three each of two types of QC samples				

This is to certify that _____ has been an analyst in the GC volatile department and has demonstrated competency at the preceeding tasks for the following methods (list below):

_____

Items found to be not satisfactory at the 3 month interval should be discussed with the analyst and further training done. Not satisfactory items should be re-evaluated at the end of the 6 month probationary period.

Laucks Testing Labs
Fuels GC Semivolatile Analyst Training Verification Checklist

Analyst Name:		Date:	Trainer:	Supervisor:	Analyst:
Documentation					
1	Able to use Standards Log				
2	Able to use Instrument Run Logs				
3	Able to use Instrument Maintenance Logs				
Methods					
4	Has read and understands SOPs for all applicable methods				
	List Method(s): _____				
5	Has read and understands EPA & State Methods				
	List Method(s): _____				
6	Has read and understands appropriate sections of GC Training Manual				
Instrument Operation/Maintenance					
7	Knows location and use of Instrument Manuals				
8	Knows basic GC theory				
9	Able to use GC Control Pad to set temperature program				
10	Able to use Autosampler Control Pad to set injection program				
11	Able to change syringe, septa & injection port liner				
12	Able to trim/change columns & perform leak check				
13	Able to measure and set carrier and makeup gas flows				
14	Able to bake column/injectors/detectors				
15	**NON-ROUTINE:** *Able to change detectors*				
16	**NON-ROUTINE:** *Able to perform total system cleaning*				
Analytical Performance					
17	Able to prepare standards & pass standard QC acceptance criteria				
18	Able to analyze RTM standard and set up elution range				
19	Able to analyze and generate acceptable calibration curve				
20	Able to analyze CCVs and apply QC acceptance criteria				
21	Applies acceptance criteria for surrogates and spikes				
22	Able to set up analytical runs & acquire data				
23	Able to get information on samples/analyses (test codes, MDLs, etc.)				
24	Able to quantitate an analytical batch (standards, CCVs, QC & samples)				
25	Knows reanalysis and reextraction criteria				
26	Able to perform sample dilutions (obtaining linear results)				
27	Knows correct reporting limits for method(s)				
28	Knows corrective action & documentation for out of control QC events				
29	Able to produce a data package (In-house and SW-846)				
Method Validation ***(complete one or more of the following)***					
30	Has successfully analyzed four P&A samples				
31	Has successfully analyzed two PE samples				
32	Has successfully analyzed three each of two types of QC samples				

This is to certify that _____ has been an analyst in the GC semivolatile department and has demonstrated competency at the preceeding tasks for the following methods (list below):

_____

Items found to be not satisfactory at the 3 month interval should be discussed with the analyst and further training done. Not satisfactory items should be re-evaluated at the end of the 6 month probationary period.

Laucks Testing Labs
HPLC Semivolatile Analyst Training Verification Checklist

Analyst Name:		Date:	Trainer:	Supervisor:	Analyst:
Documentation					
1	Able to use Standards Log				
2	Able to use Instrument Run Logs				
3	Able to use Instrument Maintenance Logs				
Methods					
4	Has read and understands SOPs for all applicable methods				
	List Method(s): _____				
5	Has read and understands EPA Methods (SW846)				
	List Method(s): _____				
6	Has read and understands appropriate sections of HPLC Training Manual				
Instrument Operation/Maintenance					
7	Knows location and use of Instrument Manuals				
8	Knows basic HPLC theory				
9	Able to use solvent delivery system to set mobile phase program				
10	Able to use Autosampler Control Pad to set injection program				
11	Able to change filters and guard column				
12	Able to change columns & perform leak checks				
13	Able to measure and set mobile phase flows				
14	Able to prime pumps				
15	Able to prepare mobile phase (filter water, select correct solvent grade)				
16	Able to change Helium tank				
17	**NON-ROUTINE:** *Able to change lamps*				
18	**NON-ROUTINE:** *Able to locate the high pressure build-up*				
19	**NON-ROUTINE:** *Able to change pump seal*				
20	**NON-ROUTINE:** *Able to clean flow cell*				
Analytical Performance					
21	Able to prepare standards & pass standard QC acceptance criteria				
22	Able to analyze and generate acceptable calibration curve				
23	Able to analyze CCVs and apply QC acceptance criteria				
24	Applies acceptance criteria for surrogates and spikes				
25	Able to set up analytical runs & acquire data				
26	Able to get information on samples/analyses (test codes, MDLs, etc.)				
27	Able to quantitate an analytical batch (standards, CCVs, QC & samples)				
28	Knows how to confirm detection of analytes (peak ID, conf. col.)				
29	Knows reanalysis and reextraction criteria				
30	Able to perform sample dilutions (obtaining linear results)				
31	Knows correct reporting limits for method(s)				
32	Knows corrective action & documentation for out of control QC events				
33	Able to produce a data package (In-house and SW-846)				
Method Validation ***(complete one or more of the following)***					
34	Has successfully analyzed four P&A samples				
35	Has successfully analyzed two PE samples				
36	Has successfully analyzed three each of two types of QC samples				

This is to certify that _____ has been an analyst in the HPLC semivolatile department and has demonstrated competency at the preceeding tasks for the following methods (list below):

Items found to be not satisfactory at the 3 month interval should be discussed with the analyst and further training done. Not satisfactory items should be re-evaluated at the end of the 6 month probationary period.

Laucks Testing Labs
GC/MS Volatile Analyst Training Verification Checklist

Analyst Name:		Date:	Trainer:	Supervisor:	Analyst:
Documentation					
1	Able to use Standards Log				
2	Able to use Instrument Run Logs				
3	Able to use Instrument Maintenance Logs				
Methods					
4	Has read and understands SOPs for all applicable methods				
	List Method(s): _____				
5	Has read and understands EPA Methods (SW846, CLP, 500 & 600 series)				
	List Method(s): _____				
6	Has read and understands appropriate sections of GC Training Manual				
Instrument Operation/Maintenance					
7	Knows location and use of Instrument Manuals				
8	Knows basic GC/MS theory				
9	Able to use GC Control Pad to set temperature program				
10	Able to use Autosampler Control Pad to set analysis program				
11	Able to change syringe, septa & injection port liner				
12	Able to trim/change columns & perform leak checks				
13	Able to measure and set carrier and makeup gas flows				
14	Able to bake column/injectors/detectors				
15	**NON-ROUTINE:** *Able to clean total system including P&T and autosampler*				
16	**NON-ROUTINE:** *Able to clean source*				
Analytical Performance					
[illegible]	Able to prepare daily standards				
18	Able to inject BFB				
19	Able to tune instrument to meet method specifications				
20	Able to analyze and generate acceptable calibration curve				
21	Able to analyze CCVs and apply QC acceptance criteria				
22	Applies acceptance criteria for surrogates and spikes				
23	Able to set up analytical runs (CLP & non-CLP) & acquire data				
24	Able to get information on samples/analyses (test codes, MDLs, etc.)				
25	Able to quantitate an analytical batch(standards, CCVs, QC & samples)				
26	Knows how to confirm detection of analytes (rt, spectra confirmation)				
27	Knows reanalysis criteria				
28	Able to perform sample dilutions (obtaining linear results)				
29	Knows correct reporting limits for method(s)				
30	Knows corrective action & documentation for out of control QC events				
31	Able to produce a data package (In-house, CLP and SW-846)				
Method Validation *(complete one or more of the following)*					
32	Has successfully analyzed four P&A samples				
33	Has successfully analyzed two PE samples				
34	Has successfully analyzed three each of two types of QC samples				

This is to certify that _____ has been an analyst in the GC/MS Volatile Department and has demonstrated competency at the preceeding tasks for the following methods (list below):

Items found to be not satisfactory at the 3 month interval should be discussed with the analyst and further training done. Not satisfactory items should be re-evaluated at the end of the 6 month probationary period.

Laucks Testing Labs
Metals ICP/MS Analyst Training Verification Checklist

Analyst Name:		Date:	Trainer:	Supervisor:	Analyst:
Documentation					
1	Able to use Standards Log				
2	Able to use Instrument Run Logs				
3	Able to use Instrument Maintenance Logs				
Methods					
4	Has read and understands SOPs for all applicable methods				
	*List Method(s):*_____				
5	Has read and understands EPA & State Methods				
	*List Method(s):*_____				
6	Has read and understands appropriate sections ICP/MS Training Manual				
Instrument Operation/Maintenance					
7	Knows location and use of Instrument Manuals				
8	Knows basic ICP/MS theory				
9	Able to use the software to create a method				
10	Able to use the software to set up the autosampler table				
11	Able to perform tuning to meet method criteria				
12	Able to change the vacuum pump oil				
13	Able to change the sample introduction pump tubing				
14	**NON-ROUTINE:** *Able to clean and/or change the cone*				
15	**NON-ROUTINE:** *Able to clean and/or change the torch*				
16	**NON-ROUTINE:** *Able to clean and/or change the filters, and know locations*				
17	**NON-ROUTINE:** *Able to clean and/or change the copper seals*				
Analytical Performance					
18	Able to prepare standards & pass standard QC acceptance criteria				
19	Able to analyze and generate acceptable calibration curve				
20	Able to analyze CCVs and apply QC acceptance criteria				
21	Applies acceptance criteria for internal standards and spikes				
22	Able to set up analytical runs & acquire data				
23	Able to copy the analytical run file from the hard drive to the network				
24	Able to quantitate an analytical batch (standards, CCVs, QC & samples)				
25	Knows reanalysis and redigestion criteria				
26	Able to perform sample dilutions (obtaining linear results)				
27	Knows correct reporting limits for method(s)				
28	Knows corrective action & documentation for out of control QC events				
29	Able to fix the data file in preparation for producing data package				
Method Validation ***(complete one or more of the following)***					
30	Has successfully analyzed four P&A samples				
31	Has successfully analyzed two PE samples				
32	Has successfully analyzed three each of two types of QC samples				

This is to certify that _____ has been an analyst in the Metals ICP/MS department and has demonstrated competency at the preceeding tasks for the following methods (list below):

_____

Items found to be not satisfactory at the 3 month interval should be discussed with the analyst and further training done. Not satisfactory items should be re-evaluated at the end of the 6 month probationary period.

Laucks Testing Labs
Mercury Analyst Training Verification Checklist

Analyst Name:		Date:	Trainer:	Supervisor:	Analyst:
cumentation					
-	Able to enter standards in the logbook				
2	Able to generate an instrument run log				
3	Able to make instrument maintenance logbook entries				
Methods					
4	Has read the SOPs for all applicable methods				
	List SOP(s): LTL-7501				
5	Has read and understands EPA & State Methods				
	List Method(s): 254.2, 7470,7471				
6	Has read the appropriate sections of the FIMS 400 Instruction Manual				
Instrument Operation/Maintenance					
7	Knows location and use of Instrument Manuals				
8	Knows basic theory				
9	Able to use the software to create a method				
10	Able to use the software to set up the autosampler table				
11	Able to change the peristaltic pump tubing				
12	Able to clean the spectrophotometer windows				
Analytical Performance					
18	Able to prepare standards & pass standard QC acceptance criteria				
19	Able to analyze and generate an acceptable calibration curve				
20	Able to analyze CCVs and apply QC acceptance criteria				
22	Able to set up an analytical run & acquire data				
	Able to copy the analytical run file from the hard drive to the network				
24	Able to quantitate an analytical batch (standards, CCVs, QC & samples)				
25	Knows reanalysis and redigestion criteria				
26	Able to perform sample dilutions				
27	Knows correct reporting limits for method(s)				
28	Knows corrective action & documentation for out of control QC events				
29	Able to correct the data file in preparation for producing a data package				
Method Validation *(complete one or more of the following)*					
30	Has successfully analyzed four P&A samples				
31	Has successfully analyzed two PE samples				
32	Has successfully analyzed three each of two types of QC samples				

This is to certify that _____ has been analyzing samples by the methods stated above and has demonstrated competency at the preceeding tasks for the following methods (list below):

_____

ems found to be not satisfactory at the 3 month interval should be discussed with the analyst and further training done. Not satisfactory items should be re-evaluated at the end of the 6 month probationary period.

Laucks Testing Labs
Sample Custodian Training Verification Checklist

Employee Name:		Date:	Trainer:	Supervisor:	Trainee:
Documentation					
1	Able to use Chain of Custodies for received samples				
2	Able to use Sample Receipt, Discrepancy and Preservation Forms				
3	Able to use Internal Chain of Custody Logs				
4	Able to use Chain of Custodies for subcontracted sample analysis				
Methods					
5	Has read and understands SOPs for all applicable job responsibilities				
	List SOP(s): _____				
Sample Receipt Process					
6	Knows how to receive samples				
7	Knows SAM basics, including the use of function keys				
8	Able to create client information				
9	Able to create workorders				
10	Able to enter samples in fraction screen				
11	Able to use global jobs and client jobs				
12	Able to create and use SDGs				
13	Able to complete bottle log in SAM				
14	Knows how and where to store samples once received				
15	NON-ROUTINE: *Able to create global jobs and client jobs*				
Additional Responsibilities					
16	Able to prepare, package and ship samples to subcontract lab				
17	Able to preserve and stock bottles				
18	Able to order bottles				
19	Able to complete bottle orders				
20	Able to ship bottle orders by UPS				
21	Able to ship bottle orders by US Mail				
22	Able to ship bottle orders by Fed Ex				
23	Able to ship bottle orders by local courier				
24	Knows how to dispose of soils and document disposal				
25	Knows how to neutralize and dispose of waters and document disposal				
26	Knows and uses appropriate PPE for handling samples				
27	Able to perform sample splitting				
28	Able to perform sample preservation for volatiles methods				
Validation *(complete all of the following)*					
29	Has successfully logged in samples for one month				
30	Has successfully prepared and shipped bottles by all carriers				
31	Has successfully created client and/or global jobs				
32	Has successfully disposed of samples and documented disposal				

This is to certify that _____ has been a sample custodian in the sample receiving department and has demonstrated competency at the preceeding tasks.

Items found to be not satisfactory at the 3 month interval should be discussed with the analyst and further training done. Not satisfactory items should be re-evaluated at the end of the 6 month probationary period.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1005

Title: **Analytical Balances**

Revision history:

Number	Date
LTL-0005 R1	09/25/86
LTL-0005 R2	11/3/87
3	06/22/96
4	5/15/98
5	12/15/99

Revised by: Harry Romberg, QA Officer Date: 12-15-99

Approved by: Kathy Kreps, Laboratory Director Date: 12-15-99

Contr[illegible] [illegible]ocument
No. 20 **Assigned to:** Tetra

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APPENDIX I **10**

SAMPLE PAGE FROM A BALANCE LOGBOOK 10

1. Introduction and Scope

1.1 General

1.1.1 The most important piece of equipment in any analytical laboratory is the analytical balance. The degree of accuracy of the data is directly dependent on the accuracy of weight-prepared standards and samples. The balance should be one of the most cared for instruments in the lab. However this is not often the case.

1.1.2 The purpose of this SOP is to insure the proper use and calibration of all analytical balances in the laboratory. It involves the daily use of a standard weight check and a weekly calibration with a class "S". The results of these checks are logged in a balance logbook, thereby maintaining a record of the accuracy of that balance.

1.1.3 On an annual basis, analytical balances are cleaned and general maintenance performed by a qualified service technician. This process occurs automatically in conjunction with the service provider and Laucks purchasing and QA. It is the intent of this SOP to delineate internal calibration practices and not to provide additional specifics on externally provided service.

2. Equipment List

- Analytical Balance
- Manufacturer's Manual
- Balance Record Book
- Class "S" Weights

3. Safety Precautions

3.1 Safety

3.1.1 So as not to expose themselves or other analysts to potential harm and in order not to cross-contaminate samples, **it is critical that the individual analyst clean the balance and the balance area after each and every use of the balance**.

3.1.2 The analyst must not assume that the person using the balance before them cleaned up after themselves adequately and should check the area thoroughly before using the balance and clean up the area if necessary to maintain safety and reduce potential contamination.

3.1.3 Weighing chemicals and samples is potentially hazardous. The analyst should take every precaution to avoid contact of any of these things with the skin, eyes, or through

inhalation. In addition, the analyst should take precautions to see that nearby analysts or those using the balance afterwards are not inadvertently exposed.

4. Operation Procedure

4.1 Balance Setup

4.1.1 Most of the balances used at Laucks are of the electronic variety, although there are some mechanical balances. Although electronic balances tend to be somewhat more rugged than the mechanical variety, they are still subject to many of the same conditions which make the operation of all balances a critical component of their continued functioning.

4.1.2 The analytical balance is a fragile and delicate instrument, the operation of which is subject to shock, temperature and humidity changes. Mishandling and other insults also account for great loss in precision and accuracy (P & A). The following precautions should be observed in order to maintain and prolong the life of the balance.

4.1.3 Analytical balances should be mounted on a heavy, shockproof table, preferably one with a sufficiently large work surface. Although shock is less of a concern with electronic balances, they should still be treated with care. For virtually all of the balances currently used by Laucks, except for some of the less sensitive variety which have no leveling bubble, the balance level should be checked frequently and adjusted as necessary.

4.1.4 Balances should be located away from lab traffic and doors or windows where they might be subjected to drafts, sharp temperature changes and physical shock.

4.1.5 For mechanical balances, when the balance is not in use, the beam should be raised from the knife edges and in the lock (rest) position.

4.1.6 For all balances, nothing should be stored on the pan when the balance is not in use.

4.1.7 All doors to the weighing compartment should be closed.

4.1.8 Special precautions should be taken to avoid spillage of corrosive chemicals on the pan or inside the balance case. The interior should be kept scrupulously clean.

4.2 Balance and Weight Calibration

4.2.1 There are three levels of calibration; daily, weekly, and annual.

4.2.1.1 **Daily** - The daily calibration is done by the **first user** of the day. The user places a tare weight on the balance equivalent to a tare typically used on that balance, weighs the daily standard (a class "S" weight typical of the weight used on that balance) and

records the weight in the balance record book. If the weight is outside the limits set for the standard, it must be brought to the attention of the area supervisor and QA.

4.2.1.2 **Weekly** - The balance will be checked with a range of class S weights each week by the laboratory balance custodian. If a reading for a given weight exceeds the limits for that weight, the balance custodian will bring it to the attention of the area supervisor and QA.

4.2.1.3 **Annual** - Each balance will receive annual servicing and calibration by a qualified balance service representative.

4.2.2 The weights to be used for checking the balances are Class "S" weights or equivalent. The tare weight is not critical, except that it be accurately recorded.

4.2.2.1 The Class "S" Weights - These are the primary standards for checking the accuracy of the balance. They must be handled with care as they are calibrated and damage to the weights may result in inaccurate balance calibration. These weights must only be touched with the forceps supplied with the weights or with the clean white gloves also kept with the weights.

4.2.2.2 The class "S" weights are sent annually to a qualified weight re-certification service, currently Denver Instruments, although another qualified service is allowable. During this time the calibrations will be suspended or other Class "S" weights used (if available) until the calibrated weights return. In the case of our Seattle lab, two sets of certified weights are in use (one normally residing at the 940 building and one at the 921 building). Normally, these weights are used for calibrating balances in their respective buildings. During the annual class "S" weight checks, one set is sent to be calibrated and the entire Seattle facility uses the other weight set. When the first set is returned, the second is sent out and the entire Seattle office uses the first set until the second has been returned. This operation is coordinated annually by QA.

4.3 Responsibilities

4.3.1 The user is to ensure the following tasks are accomplished during the time he or she uses the balance:

- The balance is <u>clean</u> before use.
- The balance is <u>level</u> before use.
- The balance is <u>clean</u> and <u>level</u> after use.
- All weight has been removed and the balance lock lever has been returned to the proper position (for mechanical balances).

- In addition, all balances should be reset to zero when not in use.
- **Prior to use, the user should insure that the daily calibration check has been done**. If not, he or she must complete the task
- **After use, the user will insure the balance is clean and returned to the proper storage position.**
- The user will report any malfunction or failure of the daily check to the area supervisor.
- The user will mark and not use any balance which has failed calibration.

4.3.2 The balance custodian is the person assigned to perform the weekly calibration checks. The custodian's duties include:

- Performing the weekly calibration check
- Marking any balance which has failed the weekly check
- Informing the area supervisor of any balance which has failed the weekly calibration check.

4.3.3 The area supervisor will ensure that the following tasks are accomplished:

- Weekly and daily calibration checks are being performed. It is particularly important to ensure that if the individual assigned to perform the weekly checks (the balance custodian) is absent, that someone is trained and assigned to this duty.
- That any maintenance is performed for balances which do not meet specifications. This may include contacting others, such as QA, to actually correct the problem.
- That any malfunctioning balance or balance which has failed calibration not be used until it is functioning properly.

4.4 Daily Calibration Check

4.4.1 The first user to use the balance each day is to perform the daily calibration check.

4.4.2 The user will insure he or she is familiar with the operation of the balance according to the manufacturer's manual.

4.4.3 The user will first insure that the balance level is correct by checking the balancing bubble and adjusting the legs of the balance as required.

4.4.4 The user checks the zero of the balance. If it is off, the user will adjust it according to the manufacturer's manual.

4.4.5 The user will place a tare weight on the balance which is typical of weights used on that balance (such as an empty beaker or an empty VOA vial). The weight of the tare should be recorded, strictly for the record, and the balance zeroed on that weight, if it is a balance capable of zeroing on the tare (all electronic balances are so equipped). The weight of the tare is not a controlled value but is only used to indicate the level of the tare used.

4.4.6 A standard weight of a size commonly used on that balance must then be added and the weight relative to the tare recorded under the appropriate day of the week in the calibration logbook. He or she will also initial and date the entry (See Appendix I). The standard weight will be a class "S" weight or equivalent.

4.4.7 The daily weight, after taring, must not vary from its true value by more than the following amounts:

Balance capable of weighing to:	must not vary by more than:
0.1 gram	±0.2 gram
0.01 gram	±0.02 gram
0.001 gram	±0.002 gram
0.0001 gram	±0.0005 gram

4.4.7.1 **Example 1:** 1 gram samples are typically weighed into flasks with tare weights of 100 grams on a balance weighing to 0.0001 g. In order to perform the daily calibration check, a flask of about 100 grams is placed on the balance and the weight recorded. The balance is tared (set to zero) based on this weight. A 1.0000 gm. Class "S" weight is then placed on the balance with the flask and the weight recorded. This second weight must read within the limits of 0.9995 gm to 1.0005 gm.

4.4.7.2 **Example 2:** 30 gram samples are typically weighed into beakers with tare weights of 80 grams on a balance capable of weighing to 0.01 grams. In order to perform the daily calibration check, a beaker weighing about 80 grams is placed on the balance and the weight recorded. The balance is tared (set to zero) based on this weight. A 30.0000 gm. Class "S" weight is then placed on the balance with the flask and the weight recorded. This second weight must read within the limits of 29.98 gm to 30.02 gm.

4.4.8 If the user cannot obtain a weight within the control limits established for the standard weight, he or she will bring it to the attention of the area supervisor and QA. Nothing requiring accurate weight should be weighed on a balance that does not meet calibration specifications. Any balance exceeding criteria must be clearly marked until it can be brought into control.

4.4.9 An example logbook page is presented in Appendix I

4.5 Weekly Calibration Check

4.5.1 The balance custodian is the person responsible for performing the weekly calibration check and reporting problems to the area supervisor or QA. The custodian may be a different person in each area and it is the responsibility of the area supervisor to ensure that a capable balance custodian has been assigned to each area for which they are responsible. It is the responsibility of the custodian to insure that the weekly check is done even if they are not present, such as for vacation, etc.

4.5.2 On the first day of the week, the balance custodian will perform a calibration check on each balance in the lab to which they are assigned. The results of these checks will be recorded in each balance calibration logbook. This check will be performed using the laboratory Class "S" weights.

4.5.3 The balance custodian will locate the Class "S" weights and insure they are clean. They will be returned to their proper location immediately upon completion of the calibration checks.

4.5.4 The balance custodian will insure the balance is clean.

4.5.5 The balance custodian checks the zero on the balance. If it is off, he or she will adjust it according to the manufacturer's manual.

4.5.6 At a **minimum**, the balance custodian will weigh 3 weights over the range for which the balance is used. Additional weights should be used if the range used is large in order to span the range typically used for that balance. If a specific weight (i.e. 100 mg or 30 grams) is the most often used on that balance, that weight should be included in the range of calibration. The results will be recorded to the left of the entries for the daily calibration check on separate lines. The custodian will also sign and **date** the entry. The date must include the month, day and year (See Appendix I).

4.5.7 Criteria for the weights on the weekly calibration check are as follows:

	True value of weight			
↓Balance capable of weighing: ↓	<0.1000 - 1.0000	1.0000-9.99	10. - 50.	>50.
0.1 gram	inappropriate	±0.1	±0.2	±0.2
0.01 gram	±0.02	±0.02	±0.02	±0.02
0.001 gram	±0.002	±0.002	±0.002	±0.005
0.0001 gram	±0.0005	±0.0005	±0.0020	±0.0050

4.5.8 If the balance custodian cannot obtain a reading within the control limits established for the standard weights, he or she will bring it to the attention of the area supervisor and QA.

4.5.9 An example logbook page is presented in Appendix I

4.6 Annual Calibration Check

4.6.1 The laboratory employs a reputable outside firm to perform annual maintenance and calibration of all of the analytical balances. The current firm is North West Instrument Services but any reputable vendor may be used if first approved by QA.

5. References

ASTM Standard Method of Testing, TOP-LOADING, DIRECT READING LABORATORY SCALES AND BALANCES, Designation: E 898 - 82

APPENDIX I

Sample Page from a Balance Logbook

	TV	Class "S" Read		Mon.	Tues.	Wed.	Thurs.	Fri	S
May 4 - May 9, 1998	2.0	2.00	Tare →	54.17	54.16	54.17	54.18	54.15	
	10.0	10.00	2.0 g →	2.00	2.00	2.00	2.00	2.00	
DTR	50.0	50.00		DTR	DTR	DTR	DTR	DTR	
5-4-98	150.0	150.00		5-4-98	5-5-98	5-6-98	5-7-98	5-8-98	
May 11 - May 16, 1998	2.0	2.00	Tare →	54.17					
	10.0	10.00	2.0 g →	2.00					
DTR	50.0	50.00		DTR					
5-11-98	150.0	150.00		5-11-98					

Done once per week

Initial + Date required

Row Heading

Daily Weights

Initial + Date required

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1006

Title: Refrigerator, Freezer, and Oven Thermometer Calibration and Maintenance

Revision history:

Number	Date
1	05/01/96
2	3/20/98
3	12/21/99

Written by: Harry Romberg Date: 12-21-99
Harry Romberg, QA Officer

Approved by: Kathy Kreps Date: 12-22-99
Kathy Kreps, Laboratory Director

Controlled Document
No. 20 Assigned to: Tetra

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1. Introduction and Scope

1.1 Method Description

1.1.1 This SOP provides a description of the identification and annual calibration of thermometers used for refrigerators, freezers, and ovens and the system used to record the calibrations and locations of the thermometers.

1.1.2 This SOP also provides a description of the routine monitoring, maintenance, and corrective actions to be performed when cold storage units or ovens fail to meet control limits.

2. Equipment List

2.1 Equipment

- NIST Traceable Standard Thermometer with a range of at least -20°C to at least 110°C.
- High temperature grease pen
- Erlenmeyer flask
- ethylene glycol or equivalent solution
- thermometers covering temperatures within the operating range of the cold storage unit, oven, or other equipment of interest.
- Water

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 During the calibration and data recording the analyst will be exposed to minimal safety hazards: boiling water, hot ovens, and mercury filled thermometers. It is incumbent on the analyst to exercise due care and caution while executing this SOP. The company will provide any protective equipment or clothing needed to assure employee safety.

3.2 Waste Disposal

3.2.1 No waste is generated in this operation. If mercury-filled thermometers are broken, however, the mercury must be collected and stored with other elemental mercury so that it may either be used in other laboratory operations or disposed.

4. Thermometer Purchasing and Identification

4.1 Purchasing

4.1.1 Laucks currently has several Streck Laboratories, ERTCO and VWR Brand thermometers for cold storage monitoring but thermometers may be purchased from any reputable supplier.

4.1.2 Thermometers used for sample or standard cold storage should be accompanied by either an actual certificate of calibration against a NIST traceable thermometer or a certificate verifying that a the thermometer was calibrated in accordance with standards traceable to the National Institute of Standards and Technology and does not vary by more than one scale division. They are immersed in a vial of ethylene glycol or equivalent solution to prevent freezing and to stabilize the temperature.

4.1.3 Thermometers used for oven temperature monitoring or for other purposes need to cover the expected range of the unit or process to be measured.

4.2 Identification

4.2.1 Thermometers are received with an individual serial number imprinted on the thermometer or may be identified in any way that distinctly distinguishes them from any other thermometer. This may involve the laboratory marking the thermometer to distinguish it from others if it does not have a distinct serial number. The use of a temperature resistant grease pen may be the most suitable for this purpose but any mechanism may be used as long as the thermometer is distinctly identified.

5. Calibration

5.1 Recalibration of the standard thermometer.

5.1.1 The NIST traceable standard thermometer is recalibrated annually by sending it back to a manufacturer who has the capability to recalibrate thermometers to NIST specifications. Currently, Laucks uses the EverReady Thermometer Company (ERTCO) for recalibration services. This vendor will re-calibrate thermometers at approximately the same points at which the original calibration was performed and will take thermometers from any vendor, as long as a copy of the original calibration certificate is available.

5.1.2 Note: Microbiology NIST traceable thermometers are recalibrated at the frequency required by the Washington State Department of Health, every 3 years.

5.1.3 At a minimum, copies of the certificates of recalibration will be kept in QA files.

5.2 Recalibration of Cold Storage and Room Temperature Thermometers

5.2.1 Refrigerator thermometers are calibrated upon receipt and annually thereafter, shortly after the return of the standard thermometer from its annual recalibration. When a thermometer has been recalibrated, a small color coded sticker is attached. The color code will correspond to a particular yearly calibration. Thus an observer can easily know his/her thermometer is currently calibrated.

5.2.2 Cold storage thermometers should not be calibrated with the standard thermometer if the standard thermometer has just been used at high temperatures (such as boiling water solutions). Thermal expansion of the thermometer at radically different temperatures may result in inaccuracies. After use at high temperatures, the standard thermometer should be allowed to stabilize at room temperature for at least 24 hours before it is used for cold storage calibration.

5.2.3 Refrigerator thermometers are placed in any functional refrigerator which is not frequently opened and has adequate space and in which the temperature is between +2°C and +6°C. Freezer thermometers are placed in a functional freezer where the temperature is between -10°C and -20°C. The temperature of the refrigerator or freezer is not especially important except that it must be accurately recorded and should be in the approximate range that refrigerators or freezers are generally be kept. Cooler thermometers are already immersed in a small vial of liquid. If a thermometer is not already in such a vial it may be placed in the same Erlenmeyer flask as the standard thermometer noted below.

5.2.4 At the same time the standard thermometer is also placed in the cold storage unit. The standard thermometer is placed in the cooler in an Erlenmeyer flask of water, ethylene glycol or other suitable liquid that will not freeze at the temperature of the unit.

5.2.5 Thermometers used for temperatures near room temperature may be calibrated in the BOD incubator using the same process.

5.2.6 The thermometers are allowed to equilibrate at least overnight (12 hours) and the temperatures read and recorded. Read the temperature of the standard thermometer first, then the individual thermometers.

Note: Most thermometers are marked in 1°C or 2°C increments. This will require interpolation by the analyst to estimate intermediate temperatures.

5.2.7 Temperatures are recorded on a blank hardcopy of an Excel spreadsheet along with the cold storage unit ID and location, the thermometer ID, and the date (See appendix A). The data are later transferred to the electronic version for storage and printing. The standard thermometer and the individual thermometer readings are recorded in the log and the difference is calculated and recorded to the nearest 0.1°C.

5.2.8 The differences in temperature between the standard thermometer and the individual thermometer are calculated and recorded in the log as the "correction factor". The correction factor is calculated as the standard thermometer reading minus the individual thermometer reading so that by adding the resulting number to the individual thermometer reading will result in a "correct" temperature.

5.2.9 Correction factors are also recorded on the Cold Storage Temperature logs. An example of one of these forms is in Appendix B. The year at the top of this form changes annually without invalidating this SOP. They are located on each cold storage unit which is used for storage of environmental samples or standards.

5.2.10 When a thermometer has been recalibrated, a small color coded sticker is attached. The color code will correspond to a particular yearly calibration. A similar color coded sticker will be attached to the original hardcopy of the annual calibration log so an observer (with the log) can easily know that the thermometer is currently calibrated. Other thermometers will be marked with tape, the calibration factor noted, and initialed and dated.

5.3 Recalibration of Oven and Other Thermometers

5.3.1 Oven and other warm temperature thermometers should not be calibrated with the standard thermometer if the standard thermometer has just been used at low temperatures (such as refrigerator or freezer calibrations). Thermal expansion of the thermometer at radically different temperatures may result in inaccuracies. After use at low temperatures, the standard thermometer should be allowed to stabilize at room temperature for at least 24 hours before it is used for high temperature calibration.

5.3.2 For hot temperature calibration (generally used at temperatures too hot to touch), thermometers are calibrated in a boiling water bath. The standard and individual thermometers are inserted into a beaker of boiling water up to the immersion line. The thermometers will read a temperature slightly above 100°C if the bulbs of the thermometers are resting directly on the bottom of the beaker while the hotplate is in a heating mode. The thermometers are allowed to equilibrate for four-five minutes and the temperatures read to the nearest 1°C. Temperatures are recorded in an Excel spreadsheet along with the oven ID (if it was an oven thermometer), the thermometer ID, and the date (See appendix A).

5.3.3 The differences in temperature between the standard thermometer and the individual thermometer are calculated and recorded in the log as the "correction factor". The correction factor is calculated as the standard thermometer reading minus the individual thermometer reading so that by adding the resulting number to the individual thermometer reading will result in a "correct" temperature.

5.3.4 Correction factors may be written on the thermometer or on the unit with which that thermometer is used.

5.3.5 When a thermometer has been recalibrated, a small color coded sticker is attached. The color code will correspond to a particular yearly calibration. A similar color coded sticker will be attached to the original hardcopy of the annual calibration log so an observer (with the log) can easily know that the thermometer is currently calibrated. Other thermometers will be marked with tape, the calibration factor noted, and initialed and dated.

5.4 Recalibration of the Infrared Thermometer

5.4.1 The standard thermometer is placed in a glass Erlenmeyer flask filled with water in a cold storage unit at least overnight (12 hours).

5.4.2 The infrared thermometer is used to measure the temperature of the flask while it contains the standard thermometer.

5.4.3 The emissivity of the IR thermometer is set at the level determined in the previous calibration (if any). It should read the same temperature as the standard thermometer. If it doesn't, the emissivity is adjusted until the standard thermometer and the IR thermometer agree as closely as possible.

5.4.4 This emissivity setting, the calibration date and the person who performed the calibration are recorded on a label which is attached to the thermometer. Analysts subsequently using the thermometer must measure against a glass container and use the emissivity setting noted on the IR thermometer in order to get an accurate temperature measurement.

5.4.5 The appropriate information is also recorded on the Excel spreadsheet used for the other calibrations.

5.5 Daily Calibration Check of the Infrared Thermometer

5.5.1 Outside of its regular calibration against the NIST traceable thermometer, the infrared thermometer is checked daily at 4°C ± 2°C against a regular glass-column thermometer, which itself has been calibrated as previously discussed.

5.5.2 The regular thermometer is stored in the 940 walk-in (W01) in water in an Erlenmeyer flask. The infrared thermometer is checked against the side of the Erlenmeyer. The infrared thermometer should agree with the regular thermometer (corrected to the NIST thermometer) within ±2°C or the discrepancy further investigated.

5.5.3 Most often, a discrepancy may be corrected by cleaning the surface of the Erlenmeyer and re-taking the measurement or by replacing the IR thermometer's batteries. The latter or any other action must be recorded on the calibration logsheet. If discrepancies

persist but are consistent, it may just be necessary to fully recalibrate the infrared thermometer and adjust the approved emissivity setting. This should be coordinated with QA.

6. Monitoring Responsibilities

6.1 Use Of Calibration Logs For Cold Storage Monitoring

6.1.1 At the time of annual calibration of the individual thermometers, the correction factor is written in the space provided on the form by QA. This correction factor (as noted) is calculated such that adding the value results in a temperature corrected to the standard thermometer. This correction factor may be positive or negative depending upon whether the specific individual thermometer read low or high when compared to the standard thermometer.

6.1.2 It is not the intent of this SOP to discuss how individuals whose responsibility it is to monitor cold storage units are assigned. It is the responsibility of departmental supervisors to ensure that this activity is occurring in their areas.

6.1.3 The person monitoring each cold storage unit will add the correction factor to the value read on the thermometer when recording the temperature. The corrected temperature is reported to the nearest 0.1°C. As noted previously, temperatures are estimated between thermometer marks.

6.1.4 The person monitoring each cold storage unit will also check the thermometer to make sure their are no breaks in the column.

6.1.5 It is the responsibility of the person monitoring the particular unit to take corrective action as noted in this SOP and on the monitoring form or to see that corrective action is initiated by informing a supervisor. Any corrective actions (including simple adjustments of the cold storage unit thermostat) **must** be noted on the Cold Storage Temperature Log (Appendix B).

6.1.6 The calibration forms change quarterly, when new cold storage units are put on-line, or when unforeseen circumstances occur which call for a new form. The individual charged with monitoring the cold storage unit will transfer the cold storage ID, the cold storage unit location, the thermometer ID, and the correction factor to the new form. That person will also turn in the completed log to QA for permanent storage.

6.2 Monitoring Ovens And Other Devices

6.2.1 When oven thermometers are calibrated, QA will mark the oven with the thermometer ID and the correction factor. Log sheets are generally not used for ovens. It is the responsibility of any analyst using an oven to apply the correction factor when recording temperatures on data sheets.

6.2.2 In other cases where thermometers are calibrated, the correction factor will be kept with the thermometer or written directly on the thermometer (generally with a piece of tape). Again, it is the responsibility of the analyst to apply the correction factor when recording temperatures on data sheets.

7. Specification Limits and Corrective Actions

7.1 Thermometer Criteria

7.1.1 Thermometers should not vary by more than ±5°C from the standard thermometer reading, even though a correction factor is applied. This criterion does not apply to the infrared thermometer.

7.1.2 There should be no observable breaks in the column of any thermometer at any time during calibration or routine use.

7.2 Thermometer Corrective Actions

7.2.1 Thermometers with a break in the column must be immediately removed from use and either repaired or replaced.

7.2.2 Thermometers which read more than ±5°C from the standard thermometer reading must not be used. If they cannot be repaired or (if new) returned to the vendor, they should be disposed or clearly marked and only used for non-critical tasks. They should not be used for the storage or analysis of environmental samples or others where temperature is a critical factor.

7.3 Cold Storage Criteria

7.3.1 Refrigeration units should be in the temperature range of 4°C ± 2°C. All freezers must be <-10°C.

7.4 Cold Storage Corrective Actions

7.4.1 See Appendix B for an example Cold Storage Temperature Log. This log also contains the appropriate corrective actions in an abbreviated form.

7.4.1.1 If at all possible, actions should be taken **before** a unit exceeds temperature criteria so that samples or standards are not inadvertently stored outside the required limits for any significant length of time. This alleviates the far more onerous tasks of re-preparing standards or contacting clients for samples stored out-of-specifications.

7.4.2 Adjust the thermostat of the cold storage unit if necessary.

7.4.3 Defrost the cold storage unit if necessary. This may be done prior to adjusting the thermostat if there is severe icing of the unit and it is obvious that this is the cause of the temperature deviation.

7.4.4 If the above fail to correct the problem, contact the laboratory maintenance personnel, the departmental supervisor or QA to arrange for repair.

7.4.5 If it is determined that professional servicing is required this may be arranged upon direction of one of these individuals or another senior supervisor. If professional maintenance does not correct the problem, the unit may need to be replaced, again at management discretion.

7.4.6 Samples must not be stored at inappropriate temperatures. If the problem is not quickly solved, samples or standards must be transferred to another cold storage unit. If it is determined that samples were stored at inappropriate temperatures for an extended period, it may be necessary to contact clients to determine the course of action they would like us to take regarding their analyses. This should be coordinated with QA and project management. Standards which have been inappropriately stored will generally require disposal, generally at the discretion of QA and/or department managers.

7.4.7 Any corrective actions (including simple adjustments) **must** be noted on the Cold Storage Temperature Log (Appendix B).

Appendix I

Example Calibration Spreadsheet

Laucks Testing Laboratories
Thermometer Calibrations
1999

Cold Storage ID	Location	Serial No.	Cal. Date		FC-53631 NIST reading	Thermom. Reading	Correction Factor
C01	Inorganics	ERTCO 4156	05/10/1999		1.9	2.1	-0.2
C02	GC residues	none	05/10/1999		2.0	2.0	0.0
C03	extractions	B B01679	05/10/1999		2.0	1.8	0.2
C04	GC VOA	B B03987	05/10/1999		2.0	2.2	-0.2
C05	Inorganics	B02580	05/10/1999		1.9	1.5	0.4
C06	Warehouse	B B04765	05/10/1999		2.0	1.4	0.6
R02	GC Semi Stds.	B B03534	05/10/1999		2.0	1.8	0.2
R04	GC/MS whse.	B B00906	05/10/1999		2.0	1.9	0.1
R06	extractions	B B01708	05/10/1999		2.0	1.8	0.2
R07	extractions	B B04059	11/15/1999		4.0	4.0	0.0
R08	Inorganics	B03021	05/10/1999		1.9	1.8	0.1
R11	929 warehouse	B B01342	05/10/1999		2.0	2.0	0.0
W01	940 Walk-in	B B03928	05/10/1999		2.0	1.8	0.2
W02	921 Walk-in	B B01919	05/10/1999		2.0	2.1	-0.1
F03	GC semivolatiles	B B B08959	05/11/1999		-11.3	-12.0	0.7
F04	GC semivolatiles	B B B09215	05/11/1999		-11.3	-11.3	0.0
F05	GC/MS VOA	B B B06608	05/11/1999		-11.3	-12.7	1.4
F06	GC/VOA	B B B08543	05/11/1999		-11.3	-12.0	0.7
F07	GC/VOA stds.	B B B08765	05/11/1999		-11.3	-12.0	0.7
		Ertco 5236	05/11/1999		-11.3	-12.4	1.1
F08	929 warehouse	Ertco 4268	05/11/1999		-11.3	-11.3	0.0
		Ertco 5034	05/11/1999		-11.3	-12.5	1.2
Hg thermometer	Sample entry	BCR 2	05/10/1999		2.0	1.8	0.2
IR Thermometer (ITT-330)		Horiba 226099	05/10/1999		1.6	1.7	(at E=82)
spare		VWR 172101	05/10/1999		1.9	0.6	1.3
Oven/Water-bath/Other ID	**Location**	**Serial No.**	**Cal. Date**		**FC-53631 NIST reading**	**Thermom. Reading**	**Correction Factor**
VWR 1320		VWR 61019-204	06/22/1999	retired 6/22/99	101	103	-2.0
VWR 1320	main lab brown hood	F22641	06/22/1999		101	102	-1.0
Thelco		2	06/16/1999		101.0	101.5	-0.5
VWR 1310		3	06/16/1999		101.0	100.0	1.0
VWR 1330F	#4 Univ. Enterprises	L12-004	06/16/1999		101.2	100.8	0.4
VWR 1370F		5	06/16/1999		101.2	101.2	0.0
back waterbath (ASTM 1F)		VWR 02429	06/16/1999		101.2	211.5 F	2.7 F
front waterbath		VWR 61066-046	06/16/1999		101.2	97.2	4.0
VWR 1300 U (TOC rooom)		SPER Sci. 106	06/16/1999		101	102	-1.0

Laucks Testing Laboratories
Thermometer Calibrations
1999

Cold Storage ID	Location	Serial No.	Cal. Date	FC-53631 NIST reading	Thermom. Reading	Correction Factor
Pensky Martin (ASTM 9F)		VWR 61091-001	06/16/1999	100.8	213 F	0.4 F
VWR 1305U	TSS/TDS area	F 14547	06/23/1999	101	100	1.0
VWR 1300 U (Extractions)		F 14506	06/22/1999	100	97	3.0
Blue M (Extractions)		F 14669	06/23/1999	101	102	-1.0
front waterbath		Enviro-Safe 6	11/11/1999	99.5	102	-2.5
BOD thermometer		1	05/21/1999	2.6	2.8	-0.2
Napco Oven		SPER Sci.	06/16/1999	101.2	100.5	0.7
Digestion Area		Polyscience USA	06/16/1999	100.8	103	-2.2
VWP ASTM 9F		09107	06/16/1999	100.8	216 F	(-2.6 F)
ERDCO	Setaflash	1SF5531/85A038	06/16/1999	100.8	214 F	(-.6 F)
ERDCO	Setaflash	1SFA5531/151831	06/16/1999	100.8	213.4 F	0.0 F
spare		F22716	06/22/1999	100	100	0.0
spare		F22592	06/22/1999	101	98	3.0
spare		F22731	06/22/1999	101	97	4.0

Appendix II

Example Cold Storage Temperature Log

Cold Storage Temperature Log

Laucks Testing Laboratories, Inc.

Cold Storage ID #:_____ Thermometer ID:_____

Location:_____ Year: **2000** Correction Factor (*add this number when* ***recording*** *the thermometer reading)*:_____°C

Day	Month: Time	Temp.	Initials	Actions	Month: Time	Temp.	Initials	Actions	Month: Time	Temp.	Initials	Actions
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												
20												
21												
22												
23												
24												
25												
26												
27												
28												
29												
30												
31												

Record Time and Temperature in the proper blocks and initial the entry each day of normal laboratory operation.

If refrigerator temperatures exceed 4°C±2°C or if freezer temperatures are warmer than -10°C, corrective action must be taken.

Corrective action includes 1) Adjust the temperature of the thermostat 2) Defrost the refrigerator or freezer
3) Contact the appropriate laboratory maintenance personnel, the departmental supervisor, and/or the QA Officer
4) One of the above may decide that professional maintenance is necessary or even that the cold storage unit must be disposed of.

Any and all actions **MUST** be recorded on this log sheet. If there is insufficient room, mark on the back of the page with the date the action occurred.

Samples **MUST NOT** be stored in units which are not maintaining the proper temperature.

Appendix III

Example Infrared Thermometer Daily Check Log

Infrared Thermometer Daily Check Log

Laucks Testing Laboratories, Inc.

Thermometer ID: Horiba 226099 Checked against standard glass thermometer: BCR 2

Location: Sample Receiving Year: **2000** Emissivity Setting: **82**

Day	Month: Time	Glass Thermometer Temp. (°C)	IR Thermometer Temp. (°C)	Initials	Actions	Month: Time	Glass Thermometer Temp. (°C)	IR Thermometer Temp. (°C)	Initials	Actions
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										
11										
12										
13										
14										
15										
16										
17										
18										
19										
20										
21										
22										
23										
24										
25										
26										
27										
28										
29										
30										
31										

Record Time and Temperature in the proper blocks and initial the entry each day of normal laboratory operation. Q:\TEMPLATS\LTLFORMS\IR_CHK1.DOC 12/21/99

If IR thermometer exceeds ±2°C of the standard glass thermometer, corrective action must be taken. Corrective action includes

1) Change batteries 2) Clean erlenmeyer surface and read again 3) Contact the appropriate laboratory maintenance personnel, the departmental supervisor, and/or the QA Officer

4) If the IR thermometer is not working properly, the glass thermometer **must** be used.

Any and all actions **MUST** be recorded on this log sheet. If there is insufficient room, mark on the back of the page with the date the action occurred.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1007

Title: Use of Instrument Records and Logbooks

Revision history:

Number	Date
1.0	9/5/91
2	5/13/98

Revised by: Harry Romberg Date: 5-13-98
Harry Romberg, QA Officer

Approved by: Kathy Kreps Date: 5-18-98
Kathy Kreps, Laboratory Director

Controlled Document

No. 20 Assigned to: Tetra

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1. Introduction and Scope

1.1 Introduction

1.1.1 The maintenance of instrument logbooks is essential to monitoring instrument performance and throughput and in tracking analyses. It is also important to confirming instrument performance at the time of specific analyses and in monitoring ongoing or periodic performance degradation and the steps taken to correct or prevent such occurrences. Several systems are in place at Laucks, the differences being primarily dependent on the specific instrument and analysis types. This SOP will discuss what is expected in each.

1.2 Scope

1.2.1 This SOP primarily addresses instrument run log maintenance, maintenance manuals and other logs not addressed in other SOPs. Standards log, for instance, are discussed in the standards SOP, LTL-1013. Analytical balance logs are discussed in that SOP, LTL-1005. Cold storage logs are discussed in LTL-1006. Control and monitoring of logbooks and general items pertinent to all logbooks is discussed in Laucks SOP LTL-1019.

1.3 Definition of Terms

1.3.1 Logbook - Any bound or unbound document that forms a record of activities and pertinent data regarding an activity including but not limited to maintenance logs, standards logs, reagent chemical logs, analysis logs including instrument outputs (computer generated or strip chart recordings), balance and temperature logs, or any other regularly maintained record of activity.

2. Equipment List and Standards

2.1 Equipment

2.1.1 maintenance logbook, analytical run logbook (where appropriate) or other applicable logbook

2.1.2 pen (pencil is NOT allowed)

3. Operation procedures

3.1 All Logbooks

3.1.1 All logbook should be numbered and controlled according to procedures outlined in Laucks SOP LTL-1019. It is the analysts responsibility before initiating any new

logbook to ensure that the logbook has been identified and given a logbook number by QA. See LTL-1019 for further detail.

3.1.2 **NOTE:** All errors in all logbooks must be altered by a single-line crossout which must also be initialed and dated. No erasures, overwriting, white-out or multiple-line crossouts (blacking out) are acceptable.

3.1.3 **NOTE:** Empty space in logbooks must be lined out (preferably with a Z for large blocks of empty space). This mark, as with error correction, should be initialed and dated.

3.2 Maintenance Manuals

3.2.1 All instruments at Laucks from GC or GC/MS systems to ICPs, AAs, spectrophotometers, ion chromatographs, etc. have instrument maintenance manuals associated with the specific instrument.

3.2.2 Maintenance manuals are bound notebooks with the specific instrument and, if appropriate where multiple similar instruments are involved, instrument names or numbers printed on the outside cover. If there are multiple books for an instrument, which may be the case for instruments which have been in service for a long time, especially if they have required extensive, ongoing maintenance, the notebooks should be clearly numbered on the cover as #1, #2, etc.

3.2.3 As a general rule, loose leaf or 3-ring bound notebooks are not acceptable. The exception to this rule is for maintaining copies of professional service call paperwork or if specific forms have been created for monitoring maintenance activities. Such paperwork must be dated. Note of the service should still be made in the bound notebook associated with that instrument and the identifying number on the service log noted in the maintenance manual.

3.2.4 With a few basic rules, these maintenance manuals are free-form with no specific format but MUST include any and all maintenance associated with the particular instrument.

3.2.4.1 Each entry should be INITIALED by the person making the entry.

3.2.4.2 The maintenance manual must contain the DATE any service or maintenance was performed on the instrument and exactly WHAT that operation was. This includes everything from changing a part to cleaning an instrument orifice or changing a chromatographic column or instrument tubing. It should include everything from the simplest maintenance to the most complex, including any professional service calls.

3.2.4.3 Where maintenance is routine, some books use codes for the most common service operations. These codes must be clearly defined either on the front, inside cover of the maintenance manual or on the first page. If there are multiple books, these codes must be so defined in EACH book.

3.2.5 If the maintenance was performed because of a specific problem (not just routine, ongoing maintenance) the problem should be described in at least one entry in the maintenance book as well as the work performed at any one time, and the outcome of that maintenance, that is whether or not it was successful or what occurred when the work was performed.

3.2.6 In order to aid in monitoring instrument performance changes, service or equipment changes may also be noted in instrument run logs. However, this information is supplementary. ALL maintenance must be recorded in the maintenance manual.

3.3 Instrument Run-Logs

3.3.1 Instrument run-logs come in two essentially different forms, with variations depending upon the specific instrument. In any form, a copy of the daily run log must accompany the data from each laboratory workorder for any samples associated with that sequence.

3.3.2 GC, GC/MS, HPLC, GPC and other run-logs are in bound, pre-printed, sequentially page-numbered books. They are identified by the specific instrument type and, if appropriate where multiple similar instruments are involved, instrument names or numbers printed on the outside cover. If there are multiple books for an instrument, which will be the case for instruments which have been in service for very long, the notebooks should be clearly numbered on the cover as #1, #2, etc.

3.3.2.1 Run logs must identify the method being run either at the top of the page, or if more than one method is being used for any sequence, clearly marked by the sample entry. It is recognized that it is in some cases possible to use different methods, which may only be different in the way a calibration is interpreted or validated. It may even be that two methods are essentially identical. However, in these instances, the logsheet should clearly indicate for which method a particular sample is being analyzed.

3.3.2.2 Instrument run-logs should include places to record all relevant sample and data file IDs, performance criteria, sample type and size, additional comments pertinent to the specific analyses, and analyst initials. All appropriate information must be filled out and the page dated. Examples of current logbook forms (at the time of this writing) are located in Appendices I (GC/MS), II (GC and HPLC), and III (GPC). These forms should be considered examples and not as the only forms used by Laucks for this purpose. These forms may change with approval of the department manager and QA. Although this SOP

will not then be considered invalid, new example forms should be incorporated into the next revision.

3.3.3 In addition to the appropriate header information for each analytical GC, GC/MS, HPLC, GPC or other run, all of the pertinent information should be filled out for each injection.

3.3.4 The standards, samples, calibration checks, reference materials, QC samples, etc. should be listed in the order that they were analyzed.

3.3.5 Logbook information should be either completely filled out, or a logbook designed to incorporate all of the pertinent elements for that analysis so that all fields are filled in. Logbooks should contain all of the necessary information to track what analyses occurred, the processing order, and critical run parameters (such as what GC column was in use).

3.3.6 No empty space should be left between daily logbook entries. The end of the analytical sequence should be clearly marked and empty space on the page crossed out, the accepted practice being with a "Z" which covers the entire space being crossed out. This "Z" should be initialed and dated by the analyst making it.

3.3.7 The other type of run-log typically in use is the individual, loose-leaf instrument run-log printout. Where the instruments themselves don't produce such printouts, handwritten run-logs are produced by the analyst. These are the log types typically in use in the Inorganics area of the laboratory.

3.3.8 A copy of the run-log is included with each data packet associated with that run.

3.3.9 As with the bound book format, the samples, standards, calibration checks, reference materials, etc. should be identified and listed IN ORDER.

3.3.10 Information critical to identifying the analytical run (date, analyst, analysis type) must be included in the header information. If multiple analytical runs were made in one day, they must be identified as run #1, run #2, etc. If the instrument is capable of time-stamping run data, this option should be utilized, although it need not be included in the run-log itself.

3.3.11 Where possible laboratory practice is to maintain ongoing run-logs for inorganic instrumentation. The daily run-logs are included with all data. Records which do not lend themselves to being kept in a pre-printed bound logbook may be collected in a 3-ring binder in an organized format but not unbound or loose-leaf. After sufficient logs have been collected, they should be bound with the laboratory comb binder. These logs should be given QA logbook IDs as described in Laucks SOP LTL-1019.

3.4 Other Logbooks

3.4.1 The same general principals used for the above logbooks apply to any other logbook, unless otherwise defined in a specific SOP.

3.4.1.1 Entries should be initialed and dated.

3.4.1.2 Empty space between entries should be minimized

3.4.1.3 Errors and empty spaces should be properly crossed out, initialed and dated.

3.4.1.4 Pages are preferably sequentially numbered but if this is not practical, at least dated and/or time stamped.

3.4.1.5 The logbook should identify the operation being monitored.

3.4.1.6 The pages in the logbook should contain all appropriate information needed to identify the activity and all applicable spaces should be completely filled out.

3.4.1.7 The logbook should be given a QA ID number as described in LTL-1019.

Appendix I

GC/MS Run Logs

Laucks T[illegible] Labs, Inc.
GC/MS VOA [illegible]ment Run Log

IS /SS Amt: 1µl of _____ µg/ml
IS /SS Ref # : _____
Date : _____

Analyst: _____
Calibration Std Ref.: _____
Spike Sol'n Ref.: _____

624 8260 524 SIM CLP-Low CLP

#	FILE ID	SAMPLE ID	INJ. TIME	SAMPLE AMT	DF[1]	pH[2]	COMMENTS

[1] DF = 1 unless otherwise indicated.
[2] pH = 2 for waters unless otherwise noted.

Laucks Testing Laboratories

GC/MS Semivolatiles Injection Logbook

IS Std ID_____

CCV ID_____

DFTPP ID_____

Page: 5699

Date:_____

	File ID	Lab ID	Inj. Time	Sample Info	Dilution	Comments	Analys
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							

Appendix II

GC/HPLC Run Logs

Laucks Testing Labs

GC VOA Instrument Log

Analyst : _____ Date : _____

Chromatography Ref. Page : _____ Calibration Reference : _____

File #	Sample ID	pH	Sample Vol/Wt	STD ID / AMT	SUR ID	Comments

LAUCKS TESTING LABORATORIES

INSTRUMENT LOGSHEET

Analyst : _____

Date : _____

Instrument ID : _____

Column 1: _____

Injection Volume : _____ ul

Column 2: _____

Calibration Standard Reference : _____

File ID	Sample ID	DF	Comments

LAUCKS TESTING LABORATORIES

HPLC INSTRUMENT LOGSHEET

Analyst : _____ Date : _____

Instrument ID : _____ Column : _____

Injection Volume : _____ ul Solvent : _____

Calibration Standard Reference : _____

File ID	Sample ID	DF	Matrix	Comments

Appendix III

GPC Run Log

Laucks Testing Labs, Inc.
GPC Bench Sheet

Date	
Cal. Ref	
Analyst	
Case #	
SDG #	
Matrix	
Program	
Load Time	
Dump Time	
Collect Time	
Wash Time	

Operating Conditions:

N2 Pressure		
tank, high		psi
tank, low		psi
line		psi
Rinse Press.		psi
Sys. Press.		psi
Flow Rate		ml/min
Temp		deg F
Chart Speed		cm/min
Chart Full Scale		Volts
UV Detector		AUFS
Column ID		

Port	LTL Number	Client ID	Intermed Vol (ml)	Aliquot Clean (ml)	Volume Collect (ml)	Final Vol (ml)
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						

Comments:

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1008

Title: **QC Corrective Action**

Revision history:

Number	Date
5	6/22/96
4	3/3/96
3 (LTL-0008)	6/29/89
2 (LTL-0008)	5/19/87
1 (LTL-0008)	12/12/86

Written by: Harry Romberg Date: 6-25-96
Harry Romberg, Quality Assurance Officer

Approved by: Karen J Kotz Date: 6/25/96
Karen Kotz, Laboratory Director

UNCONTROLLED

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1. Introduction and Scope

1.1 Purpose

1.1.1 The purpose of this SOP is to establish a system to identify, document and resolve out-of-control events.

1.2 Scope

1.2.1 An out-of-control event may be recognized by any member of Laucks. When they occur, the analyst, supervisor and Quality Assurance work jointly to solve and correct the problem. Out-of-control events are documented using an Out-of-Control-Event form or a Corrective Action form, or in a few selected instances, on a logsheet with space specifically for such actions. Corrective action resulting from an audit is also dealt with using its own Audit Response form but this action is elucidated in an SOP specific to that process.

2. Definition of Terms

2.1 This section defines terms and acronyms as they are used in this SOP.

2.1.1 **Corrective Action**: Action taken by an individual(s) to correct a problem as evidenced by either the failure of QC criteria or a more general problem which could affect performance of an analysis, the quality of service or other activity undertaken by the laboratory.

2.1.2 **Out-of-control event**: Any occurrence or condition failing to meet Laucks QC criteria or has the potential to impact data quality.

2.1.3 **QA/QC**: Quality Assurance/Quality Control

2.1.4 **Reagent blank**: a measured volume of reagents used in a method.

2.1.5 **Method blank**: a reagent blank that undergoes a preparation (digestion, extraction, distillation, etc.) step prior to analysis.

2.1.6 **RPD**: Relative Percent Difference

2.1.7 **LCS**: Laboratory Control Sample

3. OUT-OF-CONTROL EVENT PROCEDURE

3.1 Identifying an Out-Of-Control Event

3.1.1 The following is a list of examples of out-of-control events. This is not a complete list of all possible out-of-control events and many of those listed may be different for different methods. Specific criteria are given in analytical SOPs or in other QA documents. If there is doubt about whether a situation is out-of-control and must be responded to, consult with Quality Assurance.

3.1.1.1 GC/MS instrument tune criteria failing to meet criteria

3.1.1.2 Initial calibration linearity, depending upon the method used for calibration, correlation coefficient <0.995 (<0.990 for some fuels analyses) or percent RSD failing to meet method specifications.

3.1.1.3 Daily and continuing calibration verification or calibration blanks outside acceptable ranges as defined in their respective SOPs.

3.1.1.4 **NOTE:** If any of the above instances (3.1.1.1-3.1.1.3) occurs, analysis is stopped. No sample analysis can occur until the event is back in control. A corrective action form does not need to be filled out for these instances if identified at the analyst level and corrected before any data are affected.

3.1.1.5 Matrix spike, surrogate spike or blank spike recoveries outside acceptable ranges.

3.1.1.6 Unacceptable RPD value for MS/MSD or duplicate samples.

3.1.1.7 Unacceptable values for LCS's and QC samples.

3.1.1.8 A reagent blank containing a target analyte greater than the method reporting limit.

3.1.1.9 A method blank containing interference or a target analyte at a concentration greater than or equal to the method reporting limit.

3.1.1.10 **Note:** Samples which contain target analyte levels which are greater than 20 times the blank or which contain none of the offending analyte may be considered acceptable.

3.1.1.11 A sample received, prepared or analyzed past holding time.

3.1.1.12 A sample depleted before all required analyses are completed.

3.1.1.13 An extract blown down to dryness, spilled or otherwise compromised.

3.1.1.14 Contaminated reagents and glassware.

3.1.1.15 Equipment malfunction or instrument failure, such as cold storage unit temperature outside acceptable ranges and the loss of data acquisition.

3.1.1.16 Record keeping omissions, errors, and deviations from the record keeping standard operating procedures are also out-of-control situations

3.2 Responding to an Out-Of-Control Event

3.2.1 When an out-of-control event is recognized, each individual involved with the analysis in question has an interactive role and responsibility, these are as follows:

3.2.2 Analyst:

3.2.2.1 Must be able to recognize QC failure and immediately take the proper action or, if unsure of the appropriate response, notify the supervisor and work with the supervisor and Quality Assurance to solve the problem; also maintains QC charts.

3.2.2.2 The analyst is also responsible for performing the following steps to correct the problem:

3.2.2.3 Examine all calculations for correctness

3.2.2.4 Examine bench sheets for correctness

3.2.2.5 Check instrumentation and operating conditions to preclude the possibility of malfunctions or operator error

3.2.2.6 Verify integrity of spiking solution, laboratory control sample, or calibration standard

3.2.2.7 Re-analyze the sample

3.2.2.8 Take other actions as noted in the specific analytical SOP.

3.2.2.9 If these steps do not yield acceptable results, consult the supervisor.

3.2.3 Supervisor:

3.2.3.1 Must review all analytical and QC data for reasonableness, accuracy and clerical errors; also responsible for QC charts. Some of the above duties may be assigned to others, with supervisory oversight, if those others have been trained to observe the conditions which would initiate further investigation.

3.2.3.2 In an out-of-control event, the supervisor works with the analyst and Quality Assurance to solve the problem and prevents the reporting of suspect data by stopping work on the analysis in question and insuring that all results that are suspect are repeated, if possible, after the source of the error is determined and remedied.

3.2.3.3 If corrective actions do not yield results which meet specifications, it may be determined that sufficient action has been taken. The supervisor and QA will approve of such decisions and if it is determined that the data quality could be impacted, the supervisor will ensure that appropriate comments are reported with the data to the client.

3.2.4 Quality Assurance:

3.2.4.1 The Quality Assurance Officer or designee will work with supervisory personnel and/or analysts to solve out-of-control situations which are not routinely corrected at the bench.

3.2.4.2 In the event that an out-of-control situation occurs that is unnoticed at the bench or supervisory level, such as performance failure on a blind QC sample, Quality Assurance will notify the supervisor, help identify and solve the problem where applicable, insure the work is stopped on the analysis and no suspect data is reported.

3.2.4.3 Finally the Quality Assurance Officer or designee must review and approve all corrective action reports which cannot be resolved. If corrective actions do not yield results which meet specifications, it may be determined that sufficient action has been taken. The supervisor and QA will approve of such decisions.

3.2.4.4 If it is determined that the data quality could be impacted, the supervisor will ensure that appropriate comments are reported with the data to the client and QA will review said comments.

3.2.5 Project Manager:

3.2.5.1 The Project Manager is responsible for notifying the client of out-of-control events, such as missed holding times, raised reporting limits, matrix interferences, etc. which cannot be resolved without potential impact on either the data quality, the agreed upon or routinely reported results, or the timely and expected delivery date. It is not necessary to contact the client for events which are correctable and do not impact the final data quality, holding times or turn-around unless specifically requested by the client.

3.3 Corrective Actions

3.3.1 Appropriate corrective action depends on the type of analysis, the extent of the discrepancy, and whether the event is determinant or not. The corrective action to be taken for analytical QC failures is usually described in the specific analytical method but may also be determined by either the supervisor, Quality Assurance Officer, or by both in conference, if necessary.

3.3.1.1 Some items may not necessitate direct intervention of QA where standard practices are in place for some events, where the SOP or project or program QAP itself dictates the corrective action and where the action taken is the most conservative response practical. These types of events may be considered to have automatic QA approval and may not even require the completion of any related out-of-control event forms.

3.3.2 A corrective action can be as extensive as replacing a complete lot of contaminated extraction solvent, re-extracting and re-analyzing a complete batch of samples, due to reagent blank contamination; or as simple as recalculating a series of results because a wrong dilution factor was applied. Again, the appropriate corrective action must be determined on a case by case basis.

3.3.3 Data cannot be released until the system is in control or the QC failure can be attributed to a cause other than method performance. In the event the out-of-control event is due to matrix problems in the sample, and the system remained out of control, the data is flagged and supporting documentation is released to the client.

3.3.4 Corrective actions are considered adequate when the problem has been resolved and data can be reported or other actions taken from an in-control condition. Alternatively, it may be determined that the action taken was, as a minimum, all that was required by the method or that no further action was reasonable or possible that would improve the data. In these cases, the final decision must be approved by the supervisor and QA.

3.4 Documenting an Out-Of-Control Event

3.4.1 This is accomplished by completing one of the following

- A Corrective Action (CA) Form (See Appendix 1)
- A QC_DB Report Form (for Inorganics analytical QC only, see Appendix 2)
- An Out-Of-Control Event (OOCE) Form (lab use only, see Appendix 3)
- A Sample Receipt Form (for sample receipt events, see Appendix 4)
- An Audit Finding Report Form (QA use only, not shown here, see audit SOP)
- or logged onto a form which itself includes corrective actions (example, Cold Storage Logsheet, see Appendix 5).

3.4.2 CA forms are general and are for documenting corrective action taken to correct problems not associated with a particular analytical event.

3.4.3 Out-Of-Control Event (OOCE) Forms are filled out by **technical** laboratory staff only and are designed for documenting analytical QC failures and associated corrective actions. Where other forms, such as the Inorganics QC_DB Report Form, are used to document that the QC parameters were checked, any failures of QC and the decision to perform corrective action or continue data processing must be documented on the OOCE form. The checklist may then be attached to the OOCE form for final data submission.

Note: It is not necessary for analytical staff to document actions which were taken prior to processing samples or which do not affect reported data.

3.4.4 Audit Finding Reports are responded to by the assigned individual and signed off by QA or a designated individual (see the audit SOP).

3.4.5 All OOCE and Corrective Action Forms shall be filled in completely by the person observing the event. Actions taken may be filled in by either the initiating person or the person actually performing the corrective action. The descriptions of the event and any corrective actions taken should be detailed and specific. The OOCE form provides check boxes for most analytical events.

Note: Holding time violations due to laboratory error are annotated on the OOCE form. Holding time violations occurring due to receipt of samples beyond the criteria are documented on the sample receipt form only.

3.4.6 If the corrective action taken and annotated on the OOCE Form resolves the problem and allows data to be reported which is in control, the action is complete and only needs to be signed by the individual taking action and the individual initiating the action.

3.4.7 If the corrective action taken and annotated on the OOCE Form does not resolve the event and it is determined that no further action can or will be taken, the form must be signed by the analyst, supervisor, and QA.

3.4.8 Originals of all OOCE forms must be turned into QA. Copies must be included in each SDG or workorder in validatable packages and in the first workorder in the "samples affected" column for non-validatable data packages.

3.4.9 Any corrective actions taken which could either impact data directly, help to explain analytical decisions that were made in order to resolve analytical discrepancies, or which would help in the interpretation of the final data package must also be narrated in the final report. OOCE forms must be turned in with the data and the supervisor creating the narrative comment for that area will comment on any decisions resulting from failed QC which could impact data validity or interpretation.

Appendix I

Corrective Action Form

Laucks Testing Laboratories
Corrective Action Report

1) Problem Description:

Response tasked to: _____ on _____

By: _____ Response Requested By _____

2) Cause:

3) Action Taken:

Completed by _____ on _____

☐ Corrective actions will be reviewed 30 days after completion to verify problem has been corrected.

☐ No further action necessary

Reviewed by: _____ on _____

1) Person initiating corrective action fill out Part 1 and may fill out Part 2 if they are aware of the cause
2) Original goes to person tasked with a response; one copy goes to QA Officer and another kept by person initiating corrective action
3) Person tasked completes response in Part 2 (if not previously completed) and Part 3, signs response, and returns original to person initiating action
4) Person initiating action determines if action corrects the problem and signs "Reviewed by." If action was insufficient, return to the person charged with responding without signing.
5) Completed original goes to QA Officer

Appendix 2

QC_DB Report Form

Laucks Testing Laboratories

QC_DB Report Form

Analyst_____

Checker_____

Test Code_____

		QC Exceeds Control Limit √ if yes	Corrective Action Approved By ____
PBlk	B_____96_____	☐	
MS/MSD	K_____96_____	☐	
SRM	R_____96_____	☐	
Blk Spk	S_____96_____	☐	
MS/Dup	M_____96_____	☐	
Duplicate	D_____96_____	☐	

This report validates the following work orders

Appendix 3

Out-Of-Control Event Form

OUT OF CONTROL EVENT FORM

No: _____

Date Recognized: _____
Date Occurred: _____
Method: _____
Initiated By: _____
Analyst: _____

- ☐ GC/MS VOA
- ☐ GC/MS ABN
- ☐ GC VOA
- ☐ GC non-VOA
- ☐ HPLC
- ☐ Metals
- ☐ Wet Chemistry
- ☐ Extractions
- ☐ Data Management

Samples Affected (Workorder & Sample Numbers.)

Type of Event: (*check all that apply*)

___ Holding time missed (*describe below*)
___ Blank ≥ MDL___ RL___ CRQ/DL___
___ Spike Recoveries do not meet criteria
___ Duplicate RPDs do not meet criteria
___ MS/MSD Results do not meet criteria ___%Rec ___ RPD
___ BS/BSD Results do not meet criteria ___%Rec ___ RPD
___ Analytical Spike recoveries do not meet criteria
___ Standard Additions do not meet criteria
___ LCS or Blank Spike Recoveries do not meet criteria
___ Surrogate Recoveries do not meet criteria
___ Calibration Corr. Coefficient does not meet criteria
___ Calibration Verification does not meet criteria ___ Init ___ Cont.
___ Recovery ___ Retention time ___ %D
___ Tuning fails criteria
___ ISTD fails criteria
___ Calculation/Transcription error
___ Other (explain)

_____
_____
_____
_____

Corrective Action: (*check all that apply*)

___ Repeat Calibration
___ Made new standards
___ Reanalyzed, Date: _____
___ Sample(s) Redigested/Reextracted Date: _____
___ Results Recalculated
___ Cleaned System
___ Ran Standard Additions
___ Notified Client _____
___ Other (Please explain)

_____
_____
_____
_____

Check One:

___ Original Results Reported

___ Rerun Results Reported

Notified:

___ QA

___ Client Services

Action taken By: _____ Date: _____ Reviewed by Initiator: _____ Date: _____

___ Out of Control Event Corrected By: _____

___ Corrective Actions Not Successful (signatures required) **DATA MUST BE FLAGGED AND/OR NARRATED**

Analyst: _____ Date: _____
Supervisor: _____ Date: _____
QA Department: _____ Date: _____

Distribution:
Original to QA
Copy to workorder / SDG file for all validatable packages and to first workorder on list for non-validatable data.

Appendix 4

Sample Receipt Form

Laucks Testing Laboratories, Inc.
SAMPLE RECEIPT LOG (1) CLP

P:\PM\Holly\docs\fax\ncmemo.doc12/22/94

Initial once samples are checked in_____

DATE RECEIVED:_____
TIME RECEIVED:_____
CLIENT NAME:_____
SDG #_____
COC #_____

SAMPLE LOG-IN DATE:_____
WORKORDER #:_____
CLIENT PROJECT:_____
AIRBILL ATTACHED?:(#)_____
RECEIVED BY:_____

Non-Conformance: (Check applicable item(s)) Client IDs affected:

- ☐ (1) Not enough sample sent for proper analysis. #s affected:_____
- ☐ (2) Sample Bottle received broken and/or cap not intact._____
- ☐ (3) Custody seal: Absent____ Present/Intact_____ Present/Broken _____
- ☐ (4) Any temperature out of compliance:_____
- ☐ (5) Sample received outside of holding time._____
- ☐ (6) Sample not properly preserved. pH = ___. Wrong preservative used._____
- ☐ (7) Illegible sample numbers or label missing from bottles._____
- ☐ (8) Identification on bottle same as identification on paperwork: yes:_____no:_____
- ☐ (9). Incomplete instructions received with sample(s). i.e..
- ☐ no Request for Analysis. no Chain-of-Custody._____
- ☐ (10) Samples received in improper container._____
- ☐ (11) Samples held in field before receipt by Lab. Days (specify)_____
- ☐ (12) Air Bubble(s) in ___of ____ samples for volatiles analysis._____
- ☐ (13) Other _____

CORRECTIVE ACTION: (Check applicable item(s))

		Correction action taken by: Inititals	Date
☐	(1) Client informed verbally (Client Services).	_____	
☐	(2) Client informed by memo/letter/fax (Client Services).	_____	_____
☐	(3) Sample processed "as received" (Sample Entry).	_____	_____
☐	(4) Re-sampling requested of client (Client Services).	_____	_____
☐	(5) Samples placed "on hold" until further notice (Sample Entry/Client Services).	_____	_____
☐	(6) NOTE IN NARRATIVE. See temperature/pH login sheet. (Sample Entry).	_____	_____
☐	(7) Other (Specify)_____	_____	_____

* When complete (within 24 hours of nonconformance) forward to QA. Original to be forwarded to initiator to be included in transmittal file.

Comments:

Appendix 5

Example Logsheet (Cold Storage)

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1009

Title: **Blind Spike Program**

Revision history:

Number	Date
LTL-0048 Rev1.1	05/18/92
2	06/21/96

Written by: Harry Romberg Date: 6-21-96
Harry Romberg, QA Officer

Approved by: Karen J Kotz Date: 6/21/96
Karen Kotz, Laboratory Director

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Cold Storage Temperature Log

Laucks Testing Laboratories, Inc.

Cold Storage ID #:

Location: Year: **1996** Correction Factor (*add this number when **recording** the thermometer reading*): _____ °C

Day	Month: Time	Temp.	Initials	Actions	Month: Time	Temp.	Initials	Actions	Month: Time	Temp.	Initials	Actions
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												
20												
21												
22												
23												
24												
25												
26												
27												
28												
29												
30												
31												

Record Time and Temperature in the proper blocks and initial the entry each day of normal laboratory operation. REFERFRM.DOC 5/29/96

If refrigerator temperatures exceed 4°C±2°C or if freezer temperatures are warmer than -10°C, corrective action must be taken.

Corrective action includes 1) Adjust the temperature of the thermostat 2) Defrost the refrigerator or freezer

3) Contact the appropriate laboratory maintenance personnel, the departmental supervisor, and/or the QA Officer

4) One of the above may decide that professional maintenance is necessary or even that the cold storage unit must be disposed of.

Any and all actions **MUST** be recorded on this log sheet. If there is insufficient room, mark on the back of the page with the date the action occurred.

Samples **MUST NOT** be stored in units which are not maintaining the proper temperature.

1. Introduction and Scope

1.1 Description

1.1.1 This SOP provides a description of how blind spikes are generated, what types of analyses are monitored, how results are evaluated and how Laucks handles out of specification events.

1.1.2 Materials may be from a multitude of sources. The analyst will most often be aware that the sample is a blind spike but in no case should the analyst know the "true" value of the submitted sample. On occasion, at the discretion of QA, a double blind sample may be submitted (one which the analyst does not know is an evaluation sample).

1.1.3 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Definition of Terms

1.2.1 **Blind Spike** - A proficiency sample which may or may not be known as such by the analyst but which contains a target analyte with a value which is not known.

1.2.2 **Double-Blind Spike** - A proficiency sample which is submitted to the analyst in such a way that it is thought to be a routine sample and which contains an unknown amount of target analyte.

2. Equipment List and Standards

2.1 Equipment

2.1.1 Pipets, flasks, containers etc. necessary to prepare spikes for submission.

2.2 Reagents

2.2.1 Deionized water, methylene chloride and other solvents or preservatives that may be required to prepare spikes. Some samples may be prepared by outside sources and only need to be submitted to the analyst.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances. During the preparation of blind spikes, the analyst will be exposed to a variety of reagent chemicals and solvents. In addition, preservatives contained in both reference materials and in sample bottles may pose health hazards. The health effects of these various chemicals may be ascertained by reading the appropriate material safety data sheets (MSDS). It is incumbent on the analyst to exercise due care and caution while executing this SOP. The company will provide any protective equipment or clothing needed to assure employee safety.

3.1.2 Many solvents also pose a fire hazard and should be treated with proper precaution.

3.2 Waste Disposal

3.2.1 Waste solvents are disposed in the appropriate waste solvent container.

3.2.2 No more blind spike material is used than is necessary for submittal of the sample so that it will not present a disposal hazard.

3.2.3 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on hazardous waster disposal.

4. Materials

4.1 Sources

4.1.1 Materials may be WS, WP or other materials from an external performance evaluation. Although these are not generated directly by the laboratory, they are blind samples in that the expected values and in many cases the constituents themselves are not known to the analyst beforehand.

4.1.2 Standard materials may be purchased from a vendor, such as Environmental Resource Associates (ERA), Analytical Products Group (APG), SPEX, Restek, Supelco or any other reputable vendor.

4.1.3 Materials may be purchased either as Performance Evaluation samples (values unknown to the laboratory), reference materials (values known to the laboratory), or as standard materials (values known to the laboratory). They may also be made up by supervisory or QA staff from materials of known content. In any instance, the value of the components

will be unknown to the analyst performing the analysis until completion of the evaluation.

4.2 Storage

4.2.1 Materials are stored as recommended by the manufacturer, most often at a temperature of 4°C ± 2°C. Metals will generally be stored in dilute nitric acid and need not be refrigerated.

5. Operation procedures

5.1 Requirements and Scheduling

5.1.1 These requirements may be program and/or method-specific. Laucks specific training requirements and documentation are discussed in other SOPs and in the QA Plan. This SOP is intended primarily to document the practices and evaluation of results and not to dictate the specific analyst requirements.

5.1.2 Initially (as part of being considered able to independently perform an analysis), an analyst may be required to analyze a single blind Performance Evaluation (PE) sample. The analyst must process the samples independently, without direction or assistance in order to be considered proficient.

5.1.3 On an ongoing basis, at least annually, an analyst may also be required to demonstrate continuing performance by analyzing a single blind PE sample.

5.1.4 PE results may also be used as a supplement to a method verification process in order to verify the laboratory's ability to perform a method.

5.1.5 These PE samples may be from a performance evaluation study, such as an EPA Water Pollution (WP) or Water Supply (WS) study, an independent vendor PE, such as Environmental Resource Associates (ERA) or Analytical Products Group (APG), or it may be prepared by an area supervisor from a known material. Blind PE samples will almost always be prepared as aqueous solutions except in limited circumstances, such as fuel hydrocarbons, where soil samples are periodically analyzed. ERA, APG or other sources of materials will be used where components are not present in WP, WS or other "official" PE samples. Acceptable results from programmatic samples, such as those for HAZWRAP, Army Corps of Engineers, or NFESC may be used to qualify analysts or to otherwise demonstrate performance, even though in some instances an actual value may not be provided by the agency.

5.1.6 WP and WS program samples are analyzed semiannually (WP in approximately June and November, WS in approximately April and September). Supplementary PE samples for analytes not present in these samples (such as fuels or GC/MS semivolatiles) are generally obtained from APG, ERA or a similar vendor and are generally analyzed along with remedial samples (if any) resulting from WP failures (results being obtained approximately 3 months after submittal of the WPs). Other external PE samples from programs such as NFESC, HAZWRAP, or the Army Corps of Engineers may be analyzed at the discretion of those programs but be used for evaluation. The precise schedule for submittal of all but programmatic samples is at the discretion of QA in order to meet laboratory needs to qualify analysts or methods or to meet other requirements.

5.1.7 One set of PE samples may be used to qualify several analytical staff. For instance, one person may extract a sample and be so qualified. Several analysts may process the extract independently and also be qualified. If multiple analysts do process the extract, however, there must be no collaboration between analysts until the results have been received by QA.

5.1.8 In any instance, the values of the components must not be divulged to the analyst(s) prior to analysis. Furthermore, if a PE sample contains one or more components from a multi-component analysis (such as a semivolatiles or pesticide mixture), the analytes themselves must not be divulged.

5.1.9 Blind spikes should be analyzed in at least duplicate so that reproducibility can be determined as well as recovery. All results should be reported for each determination where the analysis was otherwise in control. Evaluation of replicates is a laboratory option and is rarely required of any external performance evaluation program.

5.1.10 Blind spikes are typically determined for the following analyses (in water excepts as noted):

- ICP metals
- ICP/MS metals
- Graphite furnace metals (Pb, As, Se, Tl)
- Mercury
- GC Volatiles
- Gas/BTEX water & soil
- Diesel water & soil
- Petroleum Hydrocarbons (418.1) water & soil
- Pesticides
- GC/MS Volatiles
- GC/MS Semivolatiles

- PNAs
- Explosives
- Cyanide
- Total Organic Halogens
- Total Organic Carbon
- Phenolics
- Ion Chromatography (F, Cl, NO_3, SO_4)
- NO_3/NO_2 Automated Cd reduction
- others at the discretion of QA

5.1.11 Where other method references are very similar to those above, the same PE analysis may be considered adequate documentation for both methods. Other blind PE studies may be conducted at the discretion of QA.

5.1.12 Samples will be given a laboratory ID number and test code when they are submitted to the laboratory and should be tracked in the same manner as a routine sample. Results will be compared against vendor-supplied, method-specific, or laboratory-derived limits as noted in the Evaluation and Reporting section.

6. Evaluation and Reporting

6.1 Data Package Organization

6.1.1 Paperwork must be completed as it would for routine samples, documenting preparation, calibration, and analysis and quality control. In addition, a summary page must be completed with the results of the sample and any replicate analysis. The summary page must contain the following elements:

- Analyst
- Date of analysis
- Preparation Technician (where appropriate)
- Date Prepared
- Analysis (Method*)
- Preparation (Method*)
- Components obtained from the analysis
- Results obtained from the analysis
- Replicates (where applicable) and associated RPDs

* At the discretion of QA, analysis and preparation methods may be considered sufficiently similar to qualify for more than one reference technique.

6.2 Evaluation

6.2.1 The data will be evaluated by QA with possible assistance from other supervisory staff. Data must meet the limits supplied by the vendor, if purchased or supplied as part of a PE program. If limits are not given by the vendor, method specific limits may be adopted or the laboratory may choose to accept recoveries based on internal QC limits.

6.2.1.1 All relevant components must be identified by the analyst, although in a few limited cases, similar components react in much the same fashion (i.e. similar retention times or patterns). In these instances, at the discretion of QA, the analyst may be allowed to re-evaluate the analysis.

6.2.1.2 If the analysis is a multi-component mixture, the results may be considered acceptable if 90% of the target analytes are quantified correctly.

6.2.1.3 Replicates will most often be evaluated where recovery exceptions occur or where it is determined by QA or the area supervisor that this reproducibility is a critical part of the analyst's evaluation. They will also be evaluated if it is so specified in the reference method. In these instances, the acceptability criteria are generally either the laboratory-derived RPD(s) or the reference method-specified criteria.

6.2.1.4 At the discretion of QA, the data may also be evaluated for completeness and documentation.

6.3 Remedial Actions

6.3.1 If the limits for the analyzed material have been exceeded, that performance criterion will be considered to have not been met. In such case, the data will first be re-evaluated by the analyst. If sufficient extract/digestate remains, this may include re-analysis.

6.3.2 If, after re-evaluation, the performance criterion still has not been met, the results from the entire analysis will be evaluated and if sufficient criteria have not been met, the analyst may be required to analyze another blind PE sample.

6.3.2.1 In some cases, the quality of the vendor-supplied material may be in question. In this instance or in the case where no more of a specific material is available in a timely fashion, a second source of performance evaluation material may be used.

6.3.3 Continued failure may result in either or both examining the analysis/preparation method for discrepancies or it may require re-training of the analyst if it is determined that the method and instrumentation is functioning properly. In either case, action must be

initiated immediately to insure that accurate results are being produced for actual laboratory samples.

6.3.4 In the extreme case, it may be determined after consultation with supervisory staff and laboratory management (including QA), that no analyses can be performed using that method or that analyst until there is demonstration of adequate performance.

7. Record Keeping

7.1 Analyst and Method

7.1.1 Records for all evaluations will be maintained by QA. Analyst evaluation will be maintained in the analyst's training file. Method evaluations will be kept separately but may mirror the analyst's evaluation.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1011

Title: **Procedures for the Determination and Reporting of Detection Limits, Reporting Limits, Precision and Accuracy Studies, and Control Limits**

Revision history:

Number	Date
4	1/30/98
3	6/21/96
2	1/08/96
1.1	6/15/90

Revised by: Harry Romberg, QA Officer Date: 1-30-98

Approved by: Karen J. Kotz, Laboratory Director Date: 1/30/98

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1. Introduction and Scope

1.1 Overview

1.1.1 This SOP describes the determination of Instrument Detection Limits (IDLs), Method Detection Limits (MDLs), Precision and Accuracy Studies, the setting of Reporting Limits and the determination and use of control limits. All are defined in the definitions section of this SOP.

1.1.2 In general, detection limits are the minimum amount of a target analyte that can be measured and determined to be greater than zero with a known degree of confidence. For purposes of this SOP, the known degree of confidence for MDLs will be defined as the 99% level. IDLs are based strictly on instrument response and MDLs on a sample processed through the entire preparation process. This SOP is based on information provided in 40 CFR Part 136, Appendix B, *Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11* and in other sources such as the EPA Contract Laboratory Program (CLP) Inorganic Statement of Work (SOW) and SW846.

1.1.3 Criteria for Precision and Accuracy (P&A) Studies are generally defined in the specific published method, particularly those in SW 846. Where criteria are not so defined, Laucks has chosen to either use the criteria from similar methods or to set in-house criteria based on the judgment of senior management and QA. Where two methods are the same in technical detail and one does not provide P&A criteria, performance under the guidance of the method with specifications may be used to satisfy the performance criteria of both.

1.1.4 Control limits are determined initially for an analysis, generally using limits supplied in the method or defined by the program (such as CLP). After sufficient points have been accumulated the laboratory performs a statistical analysis of the data and computes the control limits which are based on 3x the standard deviation of recoveries (for accuracy limits) or relative percent differences (for precision limits). In some instances, warning limits may also be established using 2x the appropriate standard deviation.

1.1.5 This SOP is designed for applicability to a wide variety of sample types ranging from reagent water to solids containing the analyte. The MDL may vary as a function of sample type. Laucks rarely determines MDLs on any matrix other than soil or water. Other MDLs may be estimated based on these studies.

1.1.6 This SOP requires that a specific, detailed analytical method exist. When determining MDLs and P&As following this SOP, it is imperative that all sample processing steps included in the analytical method be included.

1.1.7 Where a specific method has requirements exceeding the requirements of this SOP, that method will take precedence. Where a reference method has stated detection limits, these are generally taken to be MDLs. This SOP is to be followed to validate a new method or to validate a change in a current method.

1.1.8 MDLs should be determined approximately annually for common procedures and as needed for procedures which may be performed on an infrequent basis.

1.1.9 PCB MDLs are to be performed for each PCB to be analyzed. At least one PCB MDL must be determined annually and all PCB MDL determinations must be performed within 3 years.

1.1.10 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis except in the case of P&A studies which are used to demonstrate the competency of the analyst.

1.2 Method Description

1.2.1 Detection Limits

1.2.1.1 For any metals method, the Instrument Detection Limit (IDL) must first be determined. The IDL may also be determined strictly for informational purposes for other methods but is not required. The IDL allows the analyst to assess the precision of the measurement system and to estimate the target concentration for the MDL study. IDLs are generally determined by analyzing 7 low-level standard replicates on 3 non-consecutive days and averaging the sample standard deviations from each of the three days.

1.2.1.2 In order to determine MDLs, a minimum of seven replicate measurements are made of a prepared sample matrix which contains approximately 1 to 5 times the estimated detection limit. A Student's t determination is made for the number of data points available, usually 7 (6 degrees of freedom), and the resulting standard deviation multiplied by that value to determine the MDL. All MDL data are entered into the laboratory MDL database.

Note: The CFR states that the recommended concentration levels used to determine the MDL be one to five times the MDL. It later implies that a level of up to 10 times the MDL is acceptable. Laucks considers up to 10 times the MDL to be an appropriate concentration although limited exceptions to this rule may be granted as long as the deviations are not great and they are approved by QA.

1.2.1.3 Reporting Limits (RLs) are set by the laboratory as limits that can be reliably reported on a consistent basis with a reasonable degree of confidence that the reported level is accurate. These limits may be set at the Practical Quantitation Limit (PQL) initially by using a multiplier times the MDL. The multiplier is often but not always defined in the method. After initial setting of the RL, it is rarely changed unless significant changes in the MDL occur which make it necessary to raise or lower the RL.

1.2.2 Precision and Accuracy (P&A) Studies are studies performed in order to demonstrate the laboratory's ability to perform a method and are also used to demonstrate analyst competency to perform the method. They generally involve the analysis of 4 replicates spiked at concentrations defined in the method. Where no method guidance is provided, the replicates should be prepared at concentrations of 10 to 50 times the MDL for each analyte. Adequate performance is most often defined in the reference method, although if the method performance has been demonstrated, analyst competency may be demonstrated in comparison to laboratory limits.

1.2.3 Control limits may be specified in a reference method or may be statistically determined by the laboratory from existing data. In general, laboratory determined limits for control samples must not exceed method specified limits. If laboratory determined limits do exceed method-specified limits, the entire system must be evaluated to improve method performance. In most instances, it is unacceptable for routine performance to exceed method-specified performance even if the laboratory is using method-specified control limits. This is because the laboratory cannot demonstrate adequate performance for all samples on a routine basis.

1.2.4 It is not uncommon for clients to specify reporting or control limits in their project quality assurance plans. As long as they are achievable (i.e. the requested RL is not lower than the laboratory MDL), Laucks will generally comply with the client's request for that particular project.

1.3 Definition of Terms

1.3.1 **Accuracy** - The degree of agreement of a measurement (of an average of measurements of the same thing), X, with an accepted reference or "true" value, T, usually expressed as

the difference between the two values, X-T, or the difference as a percentage of the reference or true value, 100*(X-T)/T, and sometimes expressed as a ratio, X/T. Accuracy is a measure of the bias in the system. Accuracy shall be calculated as follows:

$$\%R = \frac{C_s - C_u}{S} * 100$$

Where:

Cs = Concentration of spiked sample
Cu = Concentration of unspiked sample
S = Expected concentration of spike in sample
%R = Percent recovery

1.3.2 **Control Limits** - Control limits may be specified in a reference Method (either as mandatory or guidance limits), or may be developed by the laboratory using internal performance data. Control limits represent acceptance criteria for determining whether an analytical system is in control (functioning within acceptable guidelines).

1.3.3 **Control Sample** - A QC sample introduced into the analytical process to allow evaluation of the measurement system. In general, it is best to use samples of a matrix similar to the samples being analyzed, where such are available. The control sample, however, will generally be free from interferences other than those inherent to the matrix itself.

1.3.4 **Degrees of Freedom** - The number of independent estimates that could be obtained from a specific set of data. In general, for a simple set of *n* independent values,

$$df = n-1$$

1.3.5 **IDL** - Instrument detection limit - The lowest concentration of a target analyte that can be measured and known to be greater than the instrumental background with a known degree of confidence. It may be used as a starting point for selecting MDL study spiking levels.

1.3.6 **MDL** - Method detection limit - The minimum concentration of a substance that can be measured and reported with a known degree of confidence (99% for our purposes) that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

1.3.7 **Mean** - The arithmetic sum of a set of observations divided by the number of observations.

$$\frac{\sum X_i}{n}$$

Where:

X_i = sample value for replicate *i*
n is the number of replicates

1.3.8 **P & A** - Precision and Accuracy - This often refers to a study conducted to validate a method or an analyst conducting a particular method.

1.3.9 **PQL** - Practical Quantitation Limit - The limit at which it is determined that the constituent can not only be detected but be accurately quantified. This limit is usually 2 to 10 times the MDL but may be even larger depending upon the constituent and the matrix. Factors are often taken from the published method but may be set by the laboratory if published factors do not exist. These limits may also be used as the routine reporting limit (RL), unless otherwise contractually defined.

1.3.10 **Precision** - A measure of mutual agreement between individual measurements of the same property, usually under prescribed similar conditions. Precision is best expressed in terms of the standard deviation. Various measures of precision exist depending upon the "prescribed similar conditions".

1.3.11 **Reporting Limit (RL)** - A value greater than or equal to the MDL or the IDL which may be based on QA decision, the published method specifications, or project-specific requirements.

1.3.12 **Standard deviation** - A statistical measure of the variability of a set of sample observations. For the purposes of this SOP, the sample standard deviation is used. This is calculated using the formula:

$$s = \sqrt{\frac{\sum (X_i - \overline{X})^2}{n-1}}$$

Where:

s = the standard deviation estimated with n-1 degrees of freedom.
X_i = sample value for replicate *i*
$\overline{X}$ = mean of all of the replicates
n = the number of replicates

2. Equipment List and Standards

2.1 Equipment, Reagents and Standards

2.1.1 As appropriate for the given analysis.

2.1.2 Personal Computer with access to a spreadsheet program such as *Microsoft Excel* and the laboratory MDL database.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 Refer to the specific analytical SOP for appropriate safety precautions.

3.1.2 Waste Disposal

Refer to the specific analytical SOP for appropriate waste disposal practices. Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

4. Calibration and Quality Control

4.1.1 Calibration is as appropriate to the specific method. No matrix spiking or other routine QA is required.

5. Responsibilities

5.1 Analyst

5.1.1 Each analyst is responsible for verifying a valid MDL study was performed and is available for each method they perform. In addition, each organic instrument analyst is responsible for verifying a valid annual MDL was performed on each instrument for each method they perform.

5.1.2 Each analyst is responsible for producing a one-time initial demonstration of precision and accuracy.

5.1.3 A metals analyst is responsible for assuring that a quarterly IDL study is produced on each instrument.

5.1.4 Each analyst is responsible for labeling MDL and P&A studies appropriately.

5.1.5 Each analyst is responsible for turning in a legible MDL, IDL, and P&A study to their supervisor for review and approval prior to final submittal to QA.

5.1.6 All of the analyst activities should be coordinated through the area supervisor.

5.2 Supervisor or Senior Analyst

5.2.1 Each area supervisor or senior analyst is responsible for coordinating the effective completion of the required studies. This may include but not necessarily be limited to helping determine appropriate concentration levels, coordinating the completion of the study within the timeline required by the method and/or the QA department, and scheduling the study around the analytical workload.

5.2.2 It is the responsibility of the area supervisor or senior analyst to insure that the analyst is performing the study within the guidelines of the method and to perform a review of the final data prior to submission to QA. This review should include determination that appropriate spiking levels were used, that the data was properly computed and transcribed, and that any problems or concerns encountered during the study are documented. Part of this review must include the comparison of the data to method specific criteria. In other words, P&A data must be compared to established method criteria and MDLs must be compared to Reporting Limits to ensure they are no greater than the RLs.

5.2.3 It is the responsibility of the area supervisor to obtain the necessary information to update the control limits at a minimum of annually. This may be done in conjunction with QA and the LIMS/MIS department.

5.3 QA Department

5.3.1 It is the responsibility of the QA department to issue a Corrective Action notice to any department who fails to turn in acceptable MDL, IDL, or P&A studies.

5.3.2 It is the responsibility of the QA department to work with supervisors to schedule studies and to maintain files of all current and historical studies.

5.3.3 QA will review and provide the final sign-off that the study meets requirements.

5.3.4 QA will review and provide the final sign-off of reporting limits.

5.3.5 QA will bear the responsibility to maintain the statistically determined control limits and to ensure that they are within those specified in the reference method.

6. Operation procedures

6.1 General

6.1.1 All studies must be given laboratory LIMS ID numbers. Although they may be initially stored in QA, they will eventually be moved into the laboratory filing system and must have identification numbers in order to be able to retrieve the raw data. Identification numbers will almost always be assigned by QA but in the absence of the QA Officer may be assigned by authorization of QA or the Laboratory Director. All studies will use the SAM client code QC_Officer in order to better track them at a later date.

6.2 Instrumental Detection Limits (IDLs)

6.2.1 It is rarely necessary to perform actual IDL studies except for metals analyses. For metals analyses, they are performed quarterly on each instrument. Studies may be useful, however, to demonstrate instrument capabilities and as a tool for estimating the Method Detection Limit (MDL). Although IDLs may be used as estimates to determine appropriate MDL spiking levels, it is strictly prohibited to compute the actual MDLs based on IDL determinations. The following guidelines are provided for several general class of analyses, regardless of whether an IDL is required for that analysis type.

6.2.2 As with all studies, a laboratory ID number should be assigned by QA for tracking purposes. In the case of metals IDLs, the same ID number may be assigned to all of the quarterly IDLs, rather than just one per instrument.

6.2.3 Actual IDLs studies are performed according to the CLP SOW by analyzing 7 replicates of low-level standards made up in the same matrix as all standards and not including any processing steps that would not ordinarily be performed on standards. The levels of those standards should be estimated from manufacturers detection limit specifications.

6.2.4 IDLs should be performed under the same instrumental conditions as will be used to perform actual analyses.

6.2.5 IDL studies must contain the following information (not necessarily in this order) for submittal to QA.

- Laboratory ID number
- Analyst who performed the IDL study
- Instrument name and ID which will distinctly identify that instrument
- Spike level
- Measured concentration of the 7 replicates (per day)
- Standard Deviation

- Mean
- Determined IDL
- Concentration Units
- Date(s) the study was analyzed
- Analysis (i.e. ICP, GFAA, etc.)
- Analysts signature & date signed
- Supervisor or senior analyst review signature & date signed

6.2.6 Spectrophotometry

6.2.6.1 The EPA/CLP SOW for metals requires that the IDL study be run on 3 non-consecutive days at least 7 times each day. It is prepared from an acidified aqueous standard solution made up at 3 to 5 times the manufacturers suggested IDL. The sample standard deviation (n-1) for each individual set of determinations is calculated and the final IDL is calculated as 3 times the average of the standard deviations for the three days. This may be performed using any commercial spreadsheet but care must be taken to insure that it is done using the sample standard deviation (n-1) calculation. For *Microsoft Excel*, this is the =STDEV() calculation. Ten percent of the calculations must be manually verified in order to demonstrate that the spreadsheet calculations are accurate.

6.2.6.2 If other spectrophotometric method IDLs are established by analyzing standards 7 times on 3 non-consecutive days, the calculation of the IDL is performed as described above. In addition, the EPA/CLP method does not prescribe the determination of MDLs. It is standard laboratory procedure to perform an MDL study (see section 6.3) approximately annually for almost all routine methods of analysis, regardless of IDL frequency or other determinations.

6.2.7 Chromatography

6.2.7.1 The analyst should use the signal:noise method for determining concentrations to use for an IDL study. A preliminary estimate of 5x signal:noise is to be used; if necessary this will be adjusted and the study repeated.

6.2.8 Gas Chromatography/Mass Spectrophotometry

6.2.8.1 Mass spectral identification criteria are key in selecting target concentrations for the IDL study. The mass spectroscopist's experience in determining the minimum identifiable concentration must weigh heavily in selecting concentrations. All compounds must meet the spectral matching characteristics as called out in the analytical method for the IDL study to be valid.

6.3 Method Detection Limits (MDLs)

6.3.1 MDL studies must be performed annually for each method for inorganic analysis and for each method/instrument combination that will be used for organic methods.

6.3.2 MDL studies must also be performed when any major changes have been made in an instrument, such as a detector change.

6.3.3 Prior to beginning an MDL study, a laboratory workorder ID must be obtained from QA. The data generated from the study is then referenced to that workorder in the same manner as routine sample data.

6.3.4 MDL studies must contain the following information (not necessarily in this order). This will be accomplished by using the MDL database report plus an MDL Information Sheet (See Appendix 2).

- Laboratory ID number
- Analyst who performed the preparation
- Method number of the preparation (where applicable)
- Date(s) the study was prepared
- Method number of the clean-up (where applicable)
- Analyst who performed the MDL study
- Method number of the analysis
- Date(s) the study was analyzed
- Instrument name and ID which will distinctly identify that instrument; this cannot be a data "channel" from the computer system but must distinctly and uniquely identify that instrument.
- Spike level
- Measured concentration of the 7 replicates
- Standard Deviation
- Mean
- Determined MDL
- Concentration Units
- Reporting Limits (RLs)
- Analysts signature & date signed
- Supervisor or senior analyst review signature & date signed

6.3.5 The analyst must compare the MDLs with their current Reporting Limits (RLs) to ensure that they are no higher than the RLs. In fact, in most cases the MDLs should be demonstrably lower than the RLs unless there is a specific request to report down to the MDL.

6.3.6 If it is determined from the study that the reporting limits must be changed (i.e. the MDL is near to or exceeds the RL and cannot be re-determined with more appropriate results), the QA Officer and the supervisor, often in concert with the Laboratory and/or Technical Director(s), must meet to determine the appropriate course of action. Reporting limits are intended to be at a level for which method precision and accuracy can be obtained. This generally cannot be done when the RL is close to the MDL

6.3.7 In order to determine the Method Detection Limit (MDL), it is first necessary to estimate what the MDL will be in order that the appropriate spiking levels may be used. How this estimate is made is immaterial to the actual MDL determination. Methods for making this determination may include any one or a combination of the following:

- estimating based on the instrument detection limit (IDL) as determined above or by any other means
- estimating based on the previous MDL
- estimating based on 3 times the instrument signal to noise ratio
- estimating based on analyst judgment

6.3.8 A solution is then prepared and spiked into a sample matrix, which is as free as possible of interference and target analytes, at a level that will result in a sample concentration equivalent to 1 to 5 times the estimated MDL.

Note: The CFR states that the recommended concentration levels used to determine the MDL be one to five times the MDL. It later implies that a level of up to 10 times the MDL is acceptable. Although the analyst should make his/her best effort to spike at a level from 1 to 5 times the MDL, Laucks considers up to 10 times the MDL to be a sufficient concentration. Limited exceptions to this rule may be granted as long as the deviations are not great and they are approved by QA.

6.3.8.1 Spiking levels which are determined to be less than 1x or greater than 10x the MDLs should in almost all circumstances be re-analyzed at a more appropriate spiking level.

6.3.8.2 Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interference concentrations are not detected at the estimated method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species. The interference concentration is presupposed to be normally distributed in representative samples of a given matrix.

6.3.9 Preparation of Spiked Samples

6.3.9.1 The MDL is almost always determined in reagent water or clean sand. Prepare a laboratory standard containing all analytes of interest at a concentration which is at least equal to or in the same concentration range as the estimated MDL. The analyte concentration should not exceed 5x the estimated MDL but allowances may be made up to 10x the determined MDL.

6.3.9.2 It is extremely rare that Laucks will perform studies for other than reagent water or soil. Soil matrix will almost always be represented by clean blank sand except for metals analyses where even clean sand contains levels of some metals which exceed the 10x acceptance criteria. For such analyses, reagent spikes are used containing only the digestion/preparation reagents. MDLs on other matrices will generally only be performed upon specific client request.

6.3.10 Calculation of recovery statistics

Note: All values are used without correcting for native concentration. As previously mentioned, if blank correction is a part of the method, the average blank value is used for correcting analyte concentration measurements. In almost all methods, however, blank correction is forbidden.

6.3.10.1 The sample standard deviation is calculated as follows:

$$s = \sqrt{\frac{\sum (X_i - \overline{X})^2}{n-1}}$$

where:
s is the standard deviation estimated with n-1 degrees of freedom.
X_i = sample value for replicate i
$\overline{X}$ = mean of all of the replicates
n is the number of replicates

6.3.10.2 The Student's t statistic is determined for (n -1) degrees of freedom at the 99% confidence interval (CI). A Student's t table for the 99% CI is provided in Appendix 1. For most data sets, using n=7 sample readings, the t value is 3.143.

Note: In some cases, it may be determined that it is useful to prepare an additional sample so that, in case of laboratory accident, at least 7 are available for statistical analysis. Whether or not this is done, all samples analyzed **must** be used in the statistical evaluation unless there is a strong reason to reject one or more of the data sets, such as obvious contamination, abnormally poor surrogate recovery, set of values that are in obvious and significant disagreement with all of the others, or spilled sample. It is inappropriate to reject data which do not have an overriding reason to do so. The reason for rejection must be clearly documented in the data file. If more than 7 points are used in the MDL determination, the current MDL database will not accommodate the calculation. In this case, the determinations will necessarily be done using a spreadsheet program.

6.3.10.3 The MDL determination then becomes:

$$MDL = t_{99\%CI} * s$$

where:
$t_{99\%CI}$ = the Student's t value at the 99% confidence interval
s = the sample standard deviation as calculated above

6.3.10.4 The MDL, standard deviation and Student's t statistic for the appropriate number of replicates at the 99% CI are automatically calculated when using the Laucks MDL database.

6.3.11 Methodology Exceptions/Specifics

6.3.11.1 Wet Chemistry

6.3.11.2 The MDL for all titrimetric determinations is set as the value determined by 0.2 ml of titrant at the method specified titrant strength and sample aliquot size. This would include all tests such as versenate hardness, alkalinity, argentometric or mercurimetric chloride, titrimetric COD, etc. Karl-Fisher moistures would be an exception to this; the MDL is taken to the value determined by 0.05 ml of titrant, the method specified titrant strength, and sample size.

6.3.11.2.1 The MDL for all gravimetric residue determinations (total solids, total suspended solids, etc.) is set as the value determined by a weighing of 0.2 mg at the method specified sample size.

6.3.11.3 GC and Gas Chromatography/Mass Spectophotometry

6.3.11.3.1 The prime consideration in GC/MS determinations is the ability to make compound confirmation based on spectral identification criteria. For SIM methods this does not apply.

6.3.11.3.2 Likewise, for PCB and other multi-peak GC analyses, pattern recognition may also dictate what can actually be determined. For either situation, analyst interpretation may be in order to confirm actual compound identification. Such interpretation must be noted in the data.

6.4 Reporting Limits

6.4.1 Reporting Limits are generally determined in one of four ways:

- Administrative decision
- Set equivalent to the Practical Quantitation Limit (PQL)
- Project Specific Requirements
- The low standard

6.4.2 The administrative decision method is generally based on what the laboratory considers to be a limit which can be obtained on a consistent and reliable basis. Values obtained from statistical determinations of MDLs, for instance, cannot always be confirmed by spectral identification, pattern matching, standard response, or analytical spike recovery. In this instance, the laboratory may choose an RL which is more readily identifiable as a level for which a compound can be so identified and reliably quantified. Administrative decision may also be considered to be a part of the PQL option.

6.4.3 The PQL option is set as a factor times the MDL. This factor may either be set forth in the published method or it may be set by the laboratory. In order to be able to provide consistent and routine reporting limits, the laboratory will generally not reset PQLs when MDLs are re-determined unless the MDL changes by a factor of more than twofold.

6.4.3.1 If it is determined from the study that the reporting limits must be changed (i.e. the MDL is near to or exceeds the RL), the QA Officer and the supervisor, often in concert with the Laboratory Director and/or Technical Director, must meet to determine the appropriate course of action. Reporting limits are intended to be at a level for which reliable identification and reasonably accurate quantitation can be obtained. This generally cannot be done when the RL is close to the MDL.

6.4.4 Project Specific RLs are derived from project requirements and are contractually agreed upon between the laboratory and the client. In any event, the agreed upon limits **cannot** be less than the MDL or IDL.

6.4.5 On occasion, the low standard defines the RL. The decision to use this technique may be any combination of method specific requirements, laboratory decision, or project-specific requirements. In no case will the RL determined from the low standard be lower than the statistically determined MDL.

6.4.6 Reporting Limits are generally detailed in the Detection Limits Database and the LIMS system, unless set by project-specific agreement, in which case they are detailed in documents pertaining to that project and in the ProjQC database. The only persons given the capability to edit the approved limits are QA, LIMS system administrators, and the Technical or Laboratory Director. In most cases, only QA will actually perform any such editing. Note here that the EPA Contract Laboratory Program (CLP) requirements use specific contract required detection limits (CRDLs) or quantitation limits (CRQLs) and any project using the CLP methods will almost always also be reported using the CLP CRDLs or CRQLs. Any exception to the use of the CLP limits in these instances must also be noted in the ProjQC database and on any paperwork defining the details of the project.

6.5 Precision and Accuracy Studies

6.5.1 At a minimum, a one-time demonstration of precision and accuracy (P&A) must be performed for each method.

6.5.2 In some cases, it may also be required that an analyst will be required to perform a P&A study to be considered proficient and capable of independently performing a preparation or analysis.

6.5.3 P&A studies will be performed in accordance with the specific method. Where method-specific performance criteria are not specified, Laucks may choose to set criteria independently. Laucks' criteria, at a minimum, will meet those specified in a given method. Any determination to the contrary must be well documented and in direct consultation with QA and laboratory management.

6.5.4 All P&A studies must be turned in to QA after having undergone supervisory or senior analyst review.

6.5.5 All P&A studies must include the following information:

- Laboratory ID number
- Analyst who performed the preparation
- Method number of the preparation
- Date(s) the study was prepared
- Analyst who performed the analysis portion of the P&A study
- Method number of the analysis
- Date(s) the study was analyzed
- Instrument name and ID which will distinctly identify that instrument; this cannot be a data "channel" from the computer system but must distinctly and uniquely identify that instrument.
- Spike level
- Measured concentration of the 4 replicates
- Standard Deviation of the recovery tabulated against the published QA Acceptance Criteria Table, where available
- Average recovery tabulated against the published QA Acceptance Criteria Table
- Concentration Units
- Analysts signature & date signed
- Supervisor or senior analyst review signature & date signed
- Raw Data

6.5.6 The mean recovery and acceptance limits must meet the criteria given in the QC Acceptance Criteria Table at the end of each of the determinative methods, when available. Where criteria are not available Laucks may use internal acceptance criteria or defer to a similar technical method with P&A criteria and use this P&A criteria as guidance in establishing performance criteria. In the case of organic SW846 methods, if the criteria are not published in the individual method, the criteria in method 8000 (70%-130%) are followed as a guidance. In many instances, 70-130% is not achievable on a routine basis even by skilled staff. In this case, the laboratory (senior staff in conjunction with QA) may determine its own acceptance limits.

6.5.7 Blank spike analyses are the commonly accepted P&A evaluation. In most methods where criteria are defined, 4 replicates must meet method-specified criteria for the **laboratory** to be considered capable of adequate performance.

6.5.8 The individual **analyst** must be able to analyze four replicates and meet laboratory blank spike control limits to be considered competent to perform the applicable analysis. For purposes of the P&A study, the analyst may be considered qualified if 90% of the analytes in a multi-analyte analysis meet laboratory criteria as long as all analytes meet the default method-specific criteria.

6.5.9 For the laboratory to be able to claim routine performance within specified limits, all analysts performing an analysis must be capable of that level of performance. All analysts must be routinely capable of performance within method-specified criteria and will be evaluated against laboratory criteria, with further action and training in order if they are unable to routinely meet laboratory criteria.

6.6 Control Limits

6.6.1 Initially, when a new method is being implemented or there are insufficient data, the laboratory will use method-specified control limits for evaluation of data. If no such limits exist, the laboratory may elect to use specified limits from a similar method or may set default limits at the laboratory's discretion. These limits may be from the precision and accuracy study for that method. The determination for the suitability of setting any default limits not otherwise specified in a reference method is at the discretion of QA.

6.6.2 During the routine course of analysis, blank spike or laboratory control samples (LCS) and in many cases matrix spikes and matrix spike duplicates (or sample duplicates) will be analyzed. Spiking will occur at the levels specified in the respective methods where available, but will generally be somewhere in the middle of the calibration range.

6.6.3 When sufficient data have been gathered, generally at least 20 data points, the laboratory will undertake the determination of statistically-based control limits. These control limits are based on 3x the standard deviation of recoveries (for accuracy limits) or relative percent differences (for precision limits). In some instances, warning limits may also be established using 2x the appropriate standard deviation.

6.6.4 At a minimum, the control limits will be updated annually on a preparation/analysis/matrix specific basis. The number of data points and spiking levels used to obtain the new limits must be documented when forwarded to QA for approval.

6.6.5 If purchased from a commercial vendor, vendor-supplied control limits for a control sample will be considered adequate for default control limits if they are within the limits specified in the reference method. In addition, if the material is readily available and its composition does not change with every purchase, the laboratory will develop internal limits for that material. These limits may or may not be within the vendor-supplied limits but they **must** be within the method-specified limits.

6.6.6 In general, laboratory determined limits for **control samples** must not exceed method specified limits. If laboratory determined limits do exceed method-specified limits, the entire system must be evaluated to improve method performance. In most instances, it is unacceptable for routine performance to exceed method-specified performance even if the laboratory is using method-specified control limits. This is because even though the

laboratory may be demonstrating adequate performance on the control material in any specific analytical run, it cannot demonstrate adequate performance for all samples in that run on a routine basis.

6.6.7 The laboratory may also calculate limits for matrix spike and matrix spike duplicate or replicate samples. However, these limits are primarily used to demonstrate method performance on a particular sample or sample-type relative to the routine laboratory sample and exceptions to these limits will generally be allowed as long as control sample limits are met.

6.6.8 The laboratory may be called upon to utilize control limits specified in a method or in a specific contract as designated in the LIMS ProjQC database or supplementary paperwork. The laboratory's overall performance will be considered adequate if internal control limits are within those specified in the reference method. Contractually defined limits will be used for the control samples analyzed under the contract and appropriate corrective actions taken but will not be used as a guide for routine laboratory performance.

6.6.9 For any particular project, if the laboratory exhibits exceptions to the method or contract-specified criteria, appropriate corrective action must be taken. Should routine laboratory control limits be within method or contract-specified criteria, and laboratory limits are exceeded but method or contract limits are met, the data may be reported but should be flagged. Where appropriate, corrective action may still be taken at the discretion of QA.

7. Reports

7.1 Data Package Organization

7.1.1 All work, with the exception of control limit computations, is performed under laboratory workorder ID numbers.

7.1.2 All data supporting the study are provided in a standard format specific to that method. In order to save paper, some items, such as the initial calibration, etc., may be referenced to other workorders. However, it must all be easily recoverable if full documentation is required, up until the standard laboratory data disposal date. Rationalizations for interpreting the results of any study and specific detail which might impact the study should be documented in the file as well.

7.1.2.1 Data files are prefaced with a copy of the summary report containing all of the elements previously noted in this SOP. Where laboratory database reports are available, a copy of the database report must also kept on file by QA. All sign-offs will be handwritten.

8. References

40 CFR Part 136, Appendix B, *Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11*

EPA Contract Laboratory Program (CLP) Inorganics Statement of Work (SOW), ILM04.0.

EPA "600" Series Methods, section 8.1.1, 40 CFR, Part 136, App. A.

EPA SW846 "8000" Series Methods, both the general method 8000B and the specific methods

Navy Installation Restoration Laboratory Quality Assurance Guide, Naval Facilities Engineering Service Center, February 1996

Appendix I

Student's *t* Values

n	degrees of freedom	*t* value at 99% CI
2	1	31.821
3	2	6.965
4	3	4.541
5	4	3.747
6	5	3.365
7	**6**	**3.143**
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
12	11	2.718
13	12	2.681
14	13	2.650
15	14	2.624
16	15	2.602
17	16	2.583
18	17	2.567
19	18	2.552
20	19	2.539
21	20	2.528
22	21	2.518
23	22	2.508
24	23	2.500
25	24	2.492

Appendix II

MDL Information Sheet

Laucks Testing Laboratories, Inc.
MDL Information Sheet

This form must be submitted in addition to the information supplied on the SAM MDL summary form along with the supporting raw data.

SAM MDL Name: _____

SAM Workorder Number: _____

Analysis:

Analyst: _____

Analysis Method: _____

Analysis Date: _____

Instrument ID: _____

Preparation:

Prepared by: _____

Preparation Method: _____

Preparation Date: _____

Cleanup Method(s): _____

Review:

Analyst's Signature: _____

Supervisor's Signature: _____

QA Approval: _____

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1012

Title: Solvent QC Monitoring for Trace Residue Analysis

Revision history:

Number	Date
2	4/27/99
1	4/10/91

Written by: Harry Romberg Date: 4-29-99
Harry Romberg, Quality Assurance Officer

Reviewed by: Monica Carr Date: 4/29/99
Monica Carr, Organics Division Manager

Approved by: Kathy Kreps Date: 4/29/99
Kathy Kreps, Laboratory Director

Controlled Document
No. 20 Assigned to: Tetra

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1. Introduction and Scope

1.1 Description

1.1.1 The purpose of this SOP is to define the method(s) used to check and document the purity of the major solvents used for trace residue analysis at Laucks. The solvents being tested are methylene chloride, acetone, and hexane. Specific techniques and equipment used for operations such as concentration and solvent exchange are not addressed in this document.

2. Equipment List and Reagents

2.1 Equipment and Reagents

2.1.1 Other Glassware, reagents and equipment as delineated in the methods specific to the described task.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 Typical precautions should be taken when handling any solvent. Some, such as methylene chloride or freon are not flammable, but others, such as acetone and hexane are and should be treated with extreme caution. Long term health effects of solvent contact are often unknown but generally unfavorable. Breathing of ANY solvent vapor should be minimized, as should any direct skin contact, by working in a well ventilated area (in or near a hood if necessary) and by using the provided gloves and, if necessary or desired, respirator masks.

3.2 Waste Disposal

3.2.1 All waste solvents should be disposed in the appropriate waste solvent container, never in the sink or in combination with aqueous liquids.

3.2.2 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on hazardous waste disposal.

4. Operation procedures

4.1 Sequestering of Solvent

4.1.1 A new lot of acetone or methylene chloride must be sequestered by the supplier and the checking process initiated at least four weeks prior to using up the last of the previous lot

of that solvent. A lot is defined as a batch of solvent with the same manufacturers lot number. This must be done in order to ensure that the lot has been released for analytical use BEFORE the remainder of an acceptable lot has been used up. If any solvent has failed, a second bottle may be tested for the failed parameter(s) in order to ensure the failure was not due to laboratory contamination. Failure of the second test is grounds to reject that lot for use in the laboratory.

4.1.2 When a lot has been formally designated as acceptable, enough should be ordered to last approximately 2 months in order to minimize the frequency of testing necessary. Typically, the supplier will ship 10 cases of a sequestered lot of methylene chloride each week and acetone as requested. No more than 4 months supply of methylene chloride will ever be ordered, as typical methylene chloride recommended shelf-life is 6 months.

4.1.3 Alternatively, since it is unlikely that any lot will fail and to eliminate the time between acceptance and delivery, an appropriate supply (as defined above) may be ordered and sequestered at the laboratory for analysis. This is commonly done for hexane since we do not consume large quantities of this solvent. If said lot fails, however, the lot must be returned to the supplier and a new lot tested immediately. This lot MUST be kept separate from the current stock and very clearly marked so that it is not inadvertently used prior to acceptance. This distinction is the responsibility of the Extractions Supervisor. All solvent deliveries must be immediately reported to the Extractions Supervisor or designated alternate in order that this distinction be made.

4.2 Initiation, Data Handling and Record Maintenance

4.2.1 The Extractions supervisor or designated representative initiates the checking process. For any month in which any extractions solvent or other reagent QC is performed, a LIMS workorder is created. When a bottle from a new, previously untested lot of solvent is received, a sample ID number is assigned from the next available ID in the workorder. This "fraction" ID must contain the manufacturer, lot number, solvent, and tests (test codes) to be performed.

4.2.2 The three solvents which we specifically check in the extractions lab are methylene chloride, acetone, and hexane. The test codes used for these purposes are MECLAC, MSQCCK, and PXQCCK. These codes are used **only** for testing solvents and for nothing else. Other checks, such as sodium sulfate or Florisil should use the test code appropriate for the analysis for which the material will be used (8081, 8270, etc.)

4.2.2.1 Methylene chloride is checked for acidity, semivolatiles and pesticides/PCBs. The respective test codes assigned to these analyses are MECLAC, MSQCCK, and PXQCCK.

4.2.2.2 Acetone is checked for semivolatiles and pesticides/PCBs. The respective test codes assigned to these analyses are MSQCCK, and PXQCCK.

4.2.2.3 Hexane is checked only for pesticides. The respective test code assigned to this analysis is PXQCCK.

4.2.3 When testing has been completed, the lot will be officially designated as acceptable or failed by the QA Officer or Technical Director. This will be done by initialing the final report and sending a copy to the Extractions supervisor. Any lot will be considered acceptable which meets the criteria specified in Appendix I. The Extractions supervisor should be certain that a lot has been designated as acceptable prior to using it and should take whatever actions are necessary to ensure prompt analysis and acceptance before the last of the acceptable solvent has been used.

4.2.4 The data and report files will be maintained by the QA Officer. After all of the QC in the month has been closed and signed off, the data file and acceptance sheets will be filed with the regular workorder files.

4.3 Solvent Analysis

4.3.1 Methylene Chloride Acidity

4.3.1.1 0.01 N NaOH - To a 100 mL. volumetric flask, add 10 mls. of .1000 N sodium hydroxide from the buret of standardized NaOH in the Inorganics lab. Fill to the volumetric mark with deionized water, stopper, and mix very well. It takes several inversions of the flask to properly mix the solution (at least 10). This solution should be prepared immediately prior to analysis.

4.3.1.2 Neutral ethanol - Add 25 mls. of denatured ethanol to an Erlenmeyer flask. Add 2 or more drops of phenolphthalein indicator solution (1 gm. phenolphthalein/100 mls. ethanol). With a Pasteur pipet, add the .01 N NaOH solution dropwise until the ethanol turns slightly pink. Hold the flask against a white background to enhance the color. This solution should be prepared immediately prior to analysis

4.3.1.3 Add 25 mls. of the methylene chloride to be checked to the flask containing neutralized ethanol. Swirl. Do not shake too vigorously so that CO_2 from the air will not acidify the ethanol and cause a fading endpoint.

4.3.1.4 Add 900 uL of the 0.01 N NaOH. Swirl to mix well.

4.3.1.5 If the resulting color is pink, the methylene chloride passes (is not acidic). If it does not turn pink, it should be retested, preferably from a second bottle. If it fails

a second time, it should be rejected or used only for cleaning. Failing solvent should NEVER be used for extraction purposes.

4.3.1.6 A "PASS" or "FAIL" is entered into the SAM report under the associated regular SAM test code, MECLAC. If the solvent fails, residue analysis SHOULD NOT be performed until a suitable acceptable lot is determined. The Extractions supervisor should see that any such failing lot has been terminated in SAM. Data and the report, however, should still be submitted to the QA Officer.

4.3.2 Residue Checks

4.3.2.1 The residue checks are performed for EPA CLP Target Compound List (TCL) components for both pesticides/PCBs and semivolatiles (ABNs) as is appropriate for the solvent being checked.

4.3.2.2 In all cases, varying amounts of the appropriate solvent is concentrated to 1 mL. in a Kuderna-Danish concentrator. No splitting of the concentrate occurs. Surrogates are not added.

4.3.3 Methylene Chloride - $MeCl_2$ is used for both ABN and pesticide/PCB analyses. A separate 400 mL. concentration is done for each analysis.

4.3.3.1 For the pesticide/PCB analysis, hexane is added and the solvent exchanged and concentrated down to 1.0 mL., which is submitted for analysis.

4.3.3.2 For ABN analysis nothing is added and the $MeCl_2$ concentrated directly down to 1 mL and submitted for analysis.

4.3.4 Acetone - Acetone is used for both ABN and pesticide/PCB analyses. A separate 150 mL. concentration is done for each analysis.

4.3.4.1 For the pesticide/PCB analysis, hexane is added and the solvent exchanged and concentrated down to 1.0 mL., which is submitted for analysis.

4.3.4.2 For the ABN analysis, the acetone is blown down to near dryness with nitrogen and brought up to 1 mL. with $MeCl_2$ and submitted for analysis.

4.3.5 Hexane - Hexane is used only in pesticide analysis. It will be concentrated 25 mls. to 1 mL. as stated and submitted for TCL pesticide/PCB analysis.

4.3.6 Acceptance criteria are compiled in Appendix I and are based on the appropriate amounts of solvent concentrated to 1 mL. final volume. They are derived from Laucks reporting

limit criteria for acceptable blanks. The LIMS report indicates the acceptance level, the level found and signifies whether the detected level (if any) passes (OK) or fails (FAIL).

4.4 Data Package Organization

4.4.1 A copy of the signed acceptance form along with the raw data is retained by QA under the assigned laboratory number. The Extractions supervisor keeps a photocopy of the signed approval sheet in a file in the extractions lab.

Appendix I

Solvent Acceptance Criteria

Solvent Acceptance Criteria

Semivolatile Compounds	Total ng in 1 mL.
Phenol	5000
bis(2-Chloroethyl) ether	5000
2-Chlorophenol	10000
1,3-Dichlorobenzene	5000
1,4-Dichlorobenzene	5000
1,2-Dichlorobenzene	5000
2-Methylphenol	5000
2,2'oxybis(1-Chloropropane)	5000
4-Methylphenol	5000
N-Nitroso-di-n-propylamine	5000
Hexachloroethane	5000
Nitrobenzene	5000
Isophorone	5000
2-Nitrophenol	10000
2,4-Dimethylphenol	5000
bis(2-Chloroethoxy)methane	5000
2,4-Dichlorophenol	10000
1,2,4-Trichlorobenzene	5000
Naphthalene	5000
4-Chloroaniline	5000
Hexachlorobutadiene	5000
4-Chloro-3-methylphenol	5000
2-Methylnaphthalene	5000
Hexachlorocyclopentadiene	5000
2,4,6-Trichlorophenol	10000
2,4,5-Trichlorophenol	10000
2-Chloronaphthalene	5000
2-Nitroaniline	5000
Dimethylphthalate	25000
Acenaphthylene	5000
2,6-Dinitrotoluene	5000
3-Nitroaniline	5000
Acenaphthene	5000
2,4-Dinitrophenol	10000
4-Nitrophenol	10000
Dibenzofuran	5000
2,4-Dinitrotoluene	5000
Diethylphthalate	25000

Semivolatile Compounds	Total ng in 1 mL.
4-Chlorophenyl-phenyl ether	5000
Fluorene	5000
4-Nitroaniline	10000
4,6-Dinitro-2-methylphenol	10000
N-nitrosodiphenylamine	5000
4-Bromophenyl-phenylether	5000
Hexachlorobenzene	5000
Pentachlorophenol	10000
Phenanthrene	5000
Anthracene	5000
Carbazole	5000
Di-n-butylphthalate	25000
Fluoranthene	5000
Pyrene	5000
Butylbenzylphthalate	25000
3,3'-Dichlorobenzidine	10000
Benzo(a)anthracene	5000
Chrysene	5000
bis(2-Ethylhexyl)phthalate	25000
Di-n-Octylphthalate	25000
Benzo(b)fluoranthene	5000
Benzo(k)fluoranthene	5000
Benzo(a)pyrene	5000
Indendo(1,2,3-cd)pyrene	5000
Dibenz(a,h)anthracene	5000
Benzo(g,h,i)perylene	5000

Solvent Acceptance Criteria

Pesticide/PCB Compounds	Total ng in 1 mL.
alpha-BHC	5
beta-BHC	5
delta-BHC	5
gamma-BHC	5
Heptachlor	5
Aldrin	5
Heptachlor epoxide	5
Endosulfan I	5
Dieldrin	10
4,4'-DDE	10
Endrin	10
Endosulfan II	10
4,4'-DDD	10
Endosulfan sulfate	10
4,4'-DDT	10
Methoxychlor	50
Endrin ketone	10
Endrin aldehyde	10
alpha-Chlordane	5
gamma-Chlordane	5
Toxaphene	500
Aroclor-1016	100
Aroclor-1221	200
Aroclor-1232	100
Aroclor-1242	100
Aroclor-1248	100
Aroclor-1254	100
Aroclor-1260	100

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1013

Title: **Preparation, Storage, Shelf Life and Traceability Documentation of Standards and Reference Materials**

Revision history:

Number	Date
1	8/31/92
2	4/17/96
3	6/3/96

Written by: Harry Romberg, QA Officer Date: 6-6-96

Reviewed by: Monica Carr, Organics Manager Date: 6/6/96

Reviewed by: Bill Lundberg, Inorganics Manager Date: 6/6/96

Approved by: Karen Kotz, Laboratory Director Date: 6/6/96

UNCONTROLLED

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1. Introduction and Scope

1.1 Method Description

1.1.1 This SOP is intended to describe the way in which standards and reference materials are tracked, prepared, stored and maintained at Laucks, from the time of receipt of the neat or stock materials, solutions or their preparation to the point of use of the working standard. General descriptions of documentation of standard preparation may be present, it is not intended to define the actual method of preparation for each specific method. This is contained in the applicable analytical method SOP. The way in which these standards are tracked, however, is detailed along with the description of storage and shelf life guidance.

1.1.2 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described procedure of documentation.

1.2 Definition of Terms

1.2.1 Standard or Reference Material: these items are defined as any solution of an analyte at a known concentration prepared from purchased neat materials or stock solutions, or from intermediate solutions traceable to purchased materials. This includes calibration standards, independent laboratory control standards (LCS or SRM), spiking solutions, surrogate solutions, independent calibration verification standards.

2. Equipment Lists and Standards

2.1 Equipment

2.1.1 Equipment and reagents necessary for the preparation of any specific solution.

2.2 Standards

2.2.1 Standards as specified in each analytical SOP.

2.2.2 All standards must also be verified both qualitatively and quantitatively in order to satisfy EPA requirements for traceability. This may be accomplished by either (1) purchasing solutions which have been fully documented by a commercial vendor, or (2) following the recommended steps for traceability as outlined in the 3/90 CLP Organic statement of work.

2.3 Standards Logbooks

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards and reference materials including neats or solutions should be handled as if they are hazardous substances.

3.2 Waste Disposal

3.2.1 Waste segregation and disposal from the point of collection is further covered in Laucks SOP on Hazardous Waste Disposal.

4. Operation Procedures

4.1 Preparation of Organics and Inorganics Materials

4.1.1 General consideration in standard preparations include:

4.1.1.1 Determine volumes and aliquots required using the concentration calculations in Appendix 1.

4.1.1.2 Choose volumes and aliquots which minimize the number of intermediate dilutions required to obtain final working concentration considering:

- The inherent measurement error, i.e. no aliquots less than 20% of the volume of measurement device whenever possible.
- The ratio of solvent:analyte
- The amount of solution left over for disposal.

4.1.1.3 Be sure to use a solvent volume sufficient to dissolve all analytes.

4.1.1.4 The solvent used should be miscible with water when being used for sample spiking purposes. Most standards used in the extractions laboratory are prepared with methanol.

4.1.2 Proper Syringe/Pipette Technique

4.1.2.1 Choose an appropriate size syringe so that the measured volume is at least 2/3 of the total volume of the measurement device.

4.1.2.2 When selecting a pipette, choose volumetric pipettes only for the exact amount to be measured.

4.1.2.3 Always rinse a syringe (organics) at least ten times with the appropriate solvent in between measurements, and wipe the syringe with a Kim-wipe.

4.1.2.4 There should be no air bubbles. Either tap them away or discard the solution in the syringe/pipette and obtain another aliquot. Repeat this procedure as often as necessary to remove all bubbles. It may be helpful to use a GC septum with very small (<50 µl) syringes.

4.1.2.5 For organics, when delivering the measured volume to the dilution vessel, fill the vessel 1/2 - 2/3 with the solvent to be used, add the measured aliquot directly into the solvent without touching the sides of the container, and fill to volume with solvent. A sub-surface injection is preferable whenever possible.

4.1.3 When preparing stock solutions from neats, the following steps should be taken.

NOTE: 99.9% of the time, stock standards will be prepared WEIGHT per Volume. DO NOT use Volume measurements for liquids unless EXPRESSLY TOLD to do so by your SUPERVISOR.

4.1.3.1 The dilution vessel (volumetric flask) and stopper should be triple solvent rinsed (last time with the solvent to be used for standard preparation) and allowed to dry completely.

4.1.3.2 The neat is weighed, to 4 significant figures, directly into the volumetric flask and the weight is recorded (to 3 decimal places for volatiles, one less than actually weighed in order to account for possible small losses due to volatilization). Stopper before weighing to avoid compound volatilization if dealing with solvents or volatile materials.

4.1.3.3 For components other than volatiles, the volumetric flask is filled about 3/4 full with dilution solvent and shaken until analyte is completely in solution.

- If the analyte will not dissolve, the stoppered volumetric flask should be sonicated in the sonic bath until it does dissolve. (Because sonication heats the solution slightly, the solution should be allowed to cool before dilution to the

mark). Consult your supervisor if the compound is not in solution after sonication.

- The volumetric flask is diluted to the mark.
- If the analyte recrystallizes while stored in the refrigerator, the standard should be sonicated before use. Do not aliquot from a cloudy or opaque standard.
- In addition to the normal labeling of the standard, a separate label should be added indicating the need for sonication.

4.1.3.4 For volatiles, the flask is inverted and gently mixed three times after diluting to the mark.

4.2 Traceability Documentation for Organics and Inorganics Materials

4.2.1 All organic neat standard materials are logged into the NEATS database, as described in 4.2.5, when they arrive in the lab. No neat organic material should be used before it has been logged into the database. Inorganic stock materials are logged directly into the appropriate standards logbook. Examples of some NEATS database screens are provided in Appendix 3.

4.2.2 All standard, spike, or surrogate mixes which are diluted solutions, whether organic or inorganic in nature, are not logged into the database but are logged directly into the appropriate standards logbook.

4.2.3 The current controlled logbooks are identified in each area as follows:

- GC/MS Volatiles - MV# (used for standards made from neat materials, single analyte concentrates, or supplier provided standard mixes)
- GC/MS Semivolatiles - MS#
- Metals - ME#
- GC Pesticides - PX#
- GC Volatiles - VOA#
- GC & HPLC PNAs - BA#
- other GC & HPLC analyses - MA#
- Organic Extractions misc - EX#
- Technicon & Lachat Analyzers - TE#
- IR Oil and Grease - IN#

- Ion Chromatography - IC#
- TOC/TOX - OC#

NOTE 1: # in the above table indicates a sequential number, beginning with 1, with each subsequent controlled book with that analysis code having the next higher integral value.

NOTE 2: This logbook number is for tracking standards only. The logbooks also will have a QA logbook number used for controlling logbooks which is independent of the standards tracking process.

4.2.4 All purchased stocks and subsequent standard preparations must be recorded in the appropriate database or log-book.

4.2.5 Upon receipt, each purchased neat material, stock, intermediate or working solution is entered into either the database (if an organic neat material) or a standards log-book and assigned a unique LAUCKS identification number. The information entered in the database or standards logbook must include:

- Analyte(s) name and vendor product ID (vendor ID must be given to unequivocally identify exactly what was used).
- supplier name
- supplier lot number
- concentration and/or purity
- expiration date (either vendor supplied, the analytical SOP or determined from the shelf life table in Appendix 2, in order of preference)

NOTE: In the case of the metals solutions which are supplied without an expiration date, the date opened and corresponding expiration date will be added when the standard is opened based on, in order of preference, the analytical SOP or Shelf Life table in Appendix 2.

4.2.6 After each material is logged it is labeled with the LAUCKS ID, date received, date opened (if the material is to be used from the same container more than once) and expiration date (if not already on the label). The accompanying vendor Certificates of Analysis, Purity or Authenticity are labeled with the Laucks ID and filed in a controlled laboratory notebook in the laboratory area. These certificates are then archived through QA when the notebook is full.

4.2.7 Every prepared stock, intermediate or working standard solution is entered into the standard log-book and assigned a unique LAUCKS ID number. The logbook entry must include the items detailed in section 4.2.9. Each material must be labeled with LAUCKS ID number, preparation date, expiration date and preparer's initials. Other items to be included on the label are listed in section 4.3.1. Examples of typical standards logbook entries are provided in Appendix 4.

4.2.8 An example of the solution nomenclature used is a working ABN standard prepared on 11/13/91. The solution number assigned was MS 2-77-2. This label represents the following:

- MS - solution was made and used as a semivolatile mass spec standard
- 2- solution was logged into standard book #2
- 77- page number on which solution has been recorded
- 2- this denotes the second entry on page 77

4.2.9 All discrete measurements made during a standard preparation must be recorded in the log book, specifically, weights aliquots and final volumes.

Other pertinent data to be entered in the log book are as follows:

- Standard Name
- Parent material and concentration/purity
- Solvent/Diluent standard is prepared in
- Type of standard being prepared (i.e. inter-mediate, spike, working, calibration)
- Final concentration
- Date prepared/opened
- Expiration dates
- Analysts initials

4.2.10 The Laucks internal working material ID must be documented on the manual benchsheet, the analytical run-log or instrument printout to enable tracking back to the parent material. See Appendix 5 for examples of typical bench sheets with standards references.

4.3 Storage of Standards and Reference Materials

4.3.1 Always completely label solution with the following information:

- LAUCKS ID number
- Standard name
- Concentration
- Solvent/Diluent
- Technician's initials
- Date of preparation
- Expiration Date

4.3.2 Organic Standards and References Materials

4.3.2.1 Store in vial or bottle which minimizes head space.

4.3.2.2 Use amber or clear glass, screw tops with Teflon-liners when required, and store at, in order of preference, the temperature referenced in the analytical SOP or the temperature detailed below, in the assigned refrigerator.

4.3.2.3 Volatile Standards and Reference Materials

4.3.2.3.1 All standards solutions should be stored in the VOA freezer at -10°C to -20°C.

4.3.2.3.2 Most volatile standards are stored in the original ampules until used.

4.3.2.3.3 Standards are transferred to Mininert vials with Teflon lined septa for daily use and stored in the VOA freezer. When the standards are transferred, the information is recorded in the GC/MS Volatile Standards log book.

4.3.2.4 Other Volatile Standard Solutions

4.3.2.4.1 Some standards need to be prepared in the lab. Stock solutions are diluted using high purity MeOH.

4.3.2.4.2 To insure stability, standard solutions should be sealed in amber glass ampules

4.3.2.4.3 Rinse unsealed ampules with clean MeOH and place in oven to dry.

4.3.2.4.4 Cover ends of ampules with foil.

4.3.2.4.5 Dilute stock solution in high purity MeOH in a volumetric flask.

4.3.2.4.6 Mix gently.

4.3.2.4.7 Partially fill ampules with solution and recap with foil.

4.3.2.4.8 Use CO_2 to cool ampules until crystals form on sides.

4.3.2.4.9 Heat end of ampule with acetylene flame until glass begins to soften.

4.3.2.4.10 Gently pull end until seal is formed.

4.3.2.4.11 Label ampules and store in freezer.

4.3.2.4.12 Record the information in the Mass Spec VOA Standards Log Book (MV).

4.3.2.4.13 When standard solutions are used they should be transferred to Mininert cap vials with Teflon lined septa. The vials are stored in the VOA freezer until discarded.

4.3.2.5 Semivolatile Standards and Reference Materials

4.3.2.5.1 All standards solutions should be stored at a maximum temperature of 4 degrees C (± 2 degrees). Refer to the analytical SOPs for details as some analytes may drop out of solution if at cooler temperatures.

4.3.3 Inorganic Standards and Reference Materials

4.3.3.1 All metals standards are kept in a cabinet in the metals analysis lab. This is at room temperature. Expired standards that are kept for qualitative purposes are kept in the same room, in a different cabinet. These qualitative standards have a special label on the bottles denoting that they are not to be used for quantitative purposes. All other standards are kept at 4°C in a reach-in cooler in the inorganics lab. This cooler is dedicated to standards and SRMs only. No sample storage is allowed in this cooler.

4.4 Shelf Life

4.4.1 Expiration

4.4.1.1 If a parent material has an expiration date of month/year, then the material is considered usable through the end of that month. For example, 01/96, the material expires after 1/31/96. This guidance was obtained from various vendors.

4.4.1.2 All parent expiration dates MUST be entered into the standard log books and the expiration date for all resulting child materials must also be entered into the logbook and placed on the material label.

4.4.1.3 Note that no child solution may exceed the life of a parent solution or neat material. This stipulation may reduce the shelf life of a prepared solution from that listed in Appendix 2. For instance, if a stock solution is prepared from parent material that has an expiration date of 05/20/95 in 01/95, instead of having a six month shelf life (07/95) the solution will expire, 05/20/95, the same date as the parent.

4.4.1.4 See Appendix 2 for the Table of typical shelf life of standards and reference materials. This table is provided as guidance only. The vendor expiration date (if applicable) and the analytical SOP take precedence over any guidance set forth in the Table.

4.4.1.5 If a standard is past its expiration date it may be used for qualitative purposes only. The standards logbook must be edited to reflect this status and an additional label must be placed on the standard. This label must be bright in color and must clearly indicate that it is to be "Used for Qualitative Purposes Only".

5. Standard Verification

5.1 Criteria

5.1.1 Standards are to have their concentrations verified before use whenever possible. The QC'ing of the standard is to be recorded in the applicable column in the standards logbook unless they are validated in the individual analytical run (such as confirmation by another standard from an independent source). Criteria for standards acceptability are in many cases defined in individual SOPs. In instances where they are not so defined, acceptability criteria are:

- 80% - 120% for organics
- 90% - 110% for inorganics

Appendix 1

Example Calculations

1. Concentration Calculations from Neat Materials

HELPFUL hint: To keep yourself straight ALWAYS, ALWAYS include the units (mg, ml, etc.) in your calculations.

Example Calculations of Standard Concentrations:

Weight of Neat Material:	0.2500 gm
Volume of Solvent:	10 ml

To Calculate Concentration in mg/L (ppm):

1) Calculation in Steps.

A) $$0.2500gm * \frac{1000mg}{1.0g} = 250mg$$

A.1) Adjust the 250 mg for purity,

i.e. if purity = 90%, 250 mg x 0.9 = 225 mg

B $$10mls * \frac{1L}{1000mls} = 0.01L$$

C) $$\frac{225mg}{0.01L} = 22500mg / L$$

2) Calculation as a Single Step.

$$\frac{0.2500gm}{10ml} * 0.90(purity) * \frac{1000mg}{1gm} * \frac{1000ml}{1L} = 22500mg / L$$

3)

$$FC = \frac{W}{FV} * P * \text{Conversion Factors}$$

where;

W = Weight of neat material (g)
FV = Final Volume (ml)
P = Purity (%/100)
FC = Final Concentration (mg/L = ppm)

2. Intermediate and Working Standards (Standard Dilution)

$$(FC)(FV) \times 1000 = (AV)(PC)$$

where;

FC: Final Concentration(s) in standard desired. Units=µg/mL.
FV: Final volume of the prepared standard. Units=mL.
1000: Conversion factor from mL to µL
PC: Parent Concentration (standard normally containing high concentrations and is diluted to desired final concentration). Units = µg/mL.
AV: Aliquot Volume of parent standard required to achieve final concentrations desired.
Units: µL (microliter).

a) Neats to Stocks

$$\frac{Purity * 1{,}000{,}000 * W}{FV} = FC$$

where;

1,000,000 = Conversion factor from gram to microgram
W Weight used in standard prep (g)
FV Final Volume (ml)
FC µg/ml = ppm = mg/L
Purity = % Purity/100

For Example: 100% = purity of 1.0
86% = purity of 0.86

If the % purity is ≥ 97%, it is considered 100% pure for standards calculation.

Appendix 2

Shelf Life Guidelines

NOTE: *IN NO CASE, will the Laucks' expirations date EXCEED the manufacturer's expiration date.
IN NO CASE, will a child solution have an expiration date that exceeds its parents.

TYPE OF STANDARD	INORGANICS	ORGANICS EXTRACTIONS	ORGANICS INSTRUMENTATION[A]
Purchased Neat	10 Years *[1]	5 Years *[1]	5 Years *[1]
Purchased Stock Solution	12 Months *[2]	12 Months *[2]	6 Months *[2]
Prepared Stock Solution	12 Months	12 Months	6 Months
Intermediate Solution	3 Months	N/A	6 Months
Working Solution	2 weeks *[3]	6 Months	3 Months
Purchased Working Solution		6 Months	3 Months

* 1. Unless the manufacturers expiration date is less than the following, purchased neat standards shelf life will not exceed 10 years materials from the date of receipt for inorganics and 5 years from the date of receipt or 3 years from the date opened for organic materials, whichever is shorter.

*2. Unless manufacturers expiration date is less than the following, purchased stock solutions or intermediates shelf life will not exceed 1 year from the date opened.

* 3. Listed time is maximum. Specific shelf-life criteria are detailed in the individual SOPs.

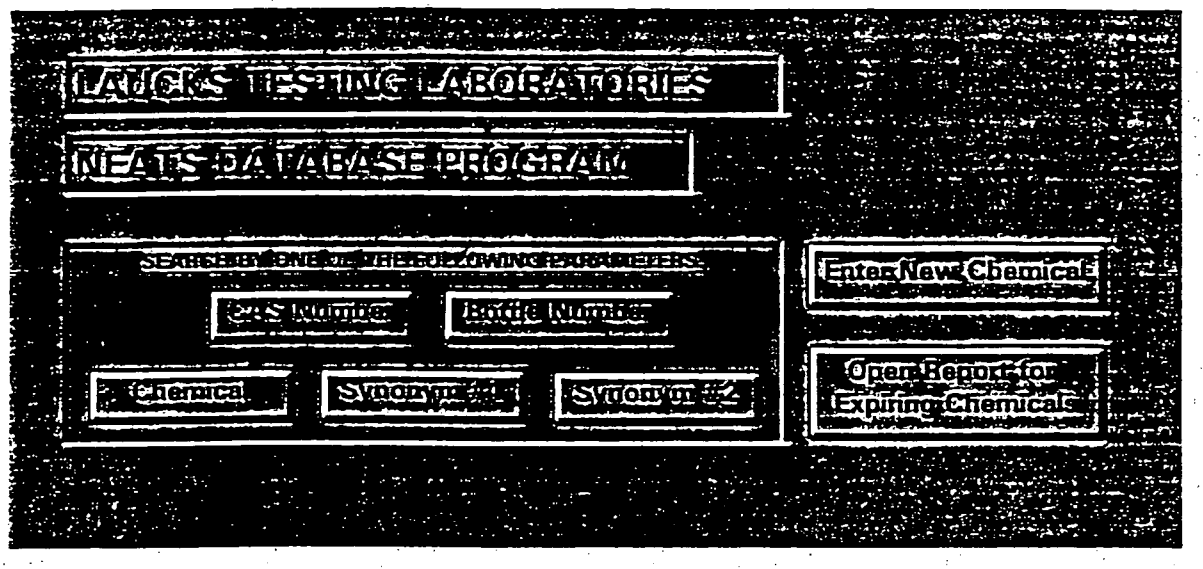
NOTE: THIS IS A GENERAL PROTOCOL. WHERE POSSIBLE, VERIFY THE INTEGRITY OF THE WORKING STANDARD SOLUTION BY MEETING THE ACCEPTANCE CRITERIA SPECIFIED IN THE ANALYTICAL SOP FROM THE KNOWN TRUE VALUE WHEN ANALYZED AGAINST AN INDEPENDENT LABORATORY CONTROL STANDARD OR A CALIBRATION CURVE.

A. Volatiles:

Method	Expiration Date
SW 846 8240 B	Stock Standards: 6 months; gases weekly if unstable, or 6 months if prepared in nitrogen. Calibration standards prepared daily
CLP OLM01.9	Stock Standards: 6 months or sooner. Stock gas standards: 2 months or sooner Secondary dilution standards: 6 months or sooner (gases & reactive compounds: monthly or sooner) Calibration standards: weekly or sooner. IS, surrogate & matrix spike: fresh spiking solution weekly or sooner. Aqueous standards: 24 hours at 4°C or 1 hour at room temperature; 12 hours if stored on autosampler.
CLP OLM0 2.0-03.1	Stock Standards: 6 months or sooner. Gases & reactive compounds: 2 months Secondary standards: 1 month or sooner for gases & reactive compounds, e.g. styrene Other purgeables: 6 months or sooner IS, surrogate & matrix spike: fresh spiking solution weekly or sooner. Calibration standards: weekly or sooner. Standard solutions stored in ampulated glass vials for 2 years from preparation date or shorter if recommended by manufacturer. Once opened, expiration dates above apply. Aqueous standards: 24 hours at 4°C or 1 hour at room temperature; 12 hours if stored on autosampler.
10/92 Low Conc. CLP	Opened stock standards: weekly Aqueous standards: 24 hours. Stock Standards: 6 months or sooner Gases stock standards: 2 months or sooner Secondary dilution standards: 6 months or sooner (gases 1 month or sooner) Working calibration standards: weekly. IS: prepare fresh spiking solution every 3 months or sooner Surrogates: prepare fresh surrogate solution every 6 months or sooner
SW 846 8260A	Stock Standards: 6 months or sooner Gases: weekly if unstable or 6 months if prepared in nitrogen Working solutions: check frequently for degradation or evaporation Calibration standards are prepared daily

Appendix 3

Neats Database Screens


LAUCKS TESTING LABORATORIES
NEATS DATABASE PROGRAM
SEARCH BY ONE OR MORE OF THE FOLLOWING PARAMETERS:
CAS Number
Bottle Number
Chemical
Synonym #1
Synonym #2
Enter New Chemicals
Open Report for Expiring Chemicals

NEATS DATA ENTRY

Chemical:	n-nitroso-diphenylamine	CAS:	86-30-6
Synonym 1:		Purity (%):	98.3
Synonym 2:		Lot #:	153-150B
Bottle #:	N1[illegible]	Source:	ChemService
Old Bottle #:		Catalog #:	O-374
Bottle:	2	Size (g):	2
Received:	4/3/96		
Expires:	10/1/2000		
Notes:	For GC/MS SVOA MS/MSD		

Previous | Next | New | Exit

Appendix 4

Logbook Examples

LAUCKS TESTING LABORATORIES, INC.
STANDARDS LOGBOOK

#	ANALYTE	ID or STOCK No.	STOCK CONC.	VOL/WT TAKEN	FINAL VOL.	CONC.	SOLVENT	PREP. DATE	INIT.	EXP. DATE	QC'D (Initials)
1	SW846 Hgl std	ME3-96-01 10/19/96	LTL-CAL-1	10 mls	100 mls		HCL 5% HNO3 1% H2O	4/2/96	KP	7/10/96	KP
		ME4-45-01 4/1/97	LTL-CAL-2	1 ml							
		ME4-32-02 3/14/97	LTL-CAL-3								
		ME3-66-05 7/10/96	1000 ppm Mo 7/10/96								
		ME3-66-09 7/10/96	1000ppm Pb 7/10/96	4 mls							
		ME3-97-08 11/17/96	1000ppm Cu 11/17/96								
		ME3-96-12	1000ppm Zn								
2	ABN SPE ICP/MS ICV3	ME4-30-01	ICP/MS KW-1	500 ul	5 mL		10% HNO3 H2O	4/3/96	ABN		
3	As	ME3-81-9 EXP 5/96	1000ppm	100 µl	5-11-96 ~~[illegible]~~ tm 100mL	1ppm	5% HNO3	4-3-96	tm	5-96	
4	ICP/MS STD1	ME4-30-02	ICP/MS	50 µl	5mL		5% HCL H2O	4/3/96 ABN	ABN		
5	STD2		Stock Std	250							
6	STD3			500							

LAUCKS TESTING LABORATORIES, INC.
STANDARDS LOGBOOK

#	ANALYTE	ID or STOCK No.	STOCK CONC.	VOL/WT TAKEN	FINAL VOL.	CONC.	SOLVENT	PREP. DATE	INIT.	EXP. DATE	QCD (Initials)
MM4-03-04 con't 4	2,4,6-TNT	M-8330-11	100 ppm	10 ul	50 ml	200 ppb	DI H2O	12/30/95	MH	04/01/96	
⊥	HMX	M-8330-4	⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥	
01	1,3,5-TNB	M-8330-12	100 ppm	10 ul	50 ml	200 ppb	Fluid TCLP #1	12/30/95	MH	04/01/96	
	2,4-DNT	M-8330-2									
	RDX	M-8330-5									
	2,4,6-TNT	M-8330-11									
⊥	HMX	M-8330-4					⊥				
02	1,3,5-TNB	M-8330-12					TCLP #2 Fluid				
	2,4,-DNT	M-8330-2									
	RDX	M-8330-5									
	2,4,6-TNT	M-8330-11									
⊥	HMX	M-8330-4	⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥	

LAUCKS TESTING LABORATORIES, INC.
STANDARDS LOGBOOK

#	ANALYTE	ID or STOCK No.	STOCK CONC.	VOL/WT TAKEN	FINAL VOL.	CONC.	SOLVENT	PREP. DATE	INIT.	EXP. DATE	QC'D (Initials)
1	IC ICV Set ~~3/11/96~~ Cl	ERA 34112	—	—	250ml	129 mg/L	—	logged in 3/18/1996	SK	Opened: 4/5/96 Exp: 4/19/97	
	F		—	—		6.47 mg/L	—				
	NO_3		—	—		8.77 mg/L	—				
	SO_4		—	—		11.0 mg/L	—				
2	Cal. Std. F	IC4.84.4	1000 ppb	500 µl	100ml	5 ppb	H_2O	3/20/96	SK	4/3/96	
	Cl	.5	1000 ppb	1000 µl		10 ppb					
	NO_2	.7	100 ppb	2000 µl		2 ppb					
	NO_3	.3	1000 ppb	500 µl		5 ppb ~~10 ppb~~ 3/20/96					
	SO_4	.6	1000 ppb	2000 µl		20 ppb					
3	NO_2 ICV	IC4.78.7	100 ppb	1000 µl	100ml	1 ppb	H_2O	3/20/96	SK	3/27/96	
4	NO_2 ICV	IC4.78.7	100 ppb	1000 µl	100ml	1 ppb	H_2O	3/25/96	SK	4/1/96	

Appendix 5

Bench Sheet Examples

As, Tl

AutoSampler Report Table: SW846 Wed 04-10-96 09:39:45 AM page 1

Table Name: SW846 Autosampler Type: TYPE TJA
Sample Positions: 257/300 QC Positions: 11/19 # Sets: 1
Rinse Station location is rack -1, pos. -1.

--- Racks ---

Rack #	Type	Usage	#Pos Left	Analyses/Pos
1	Aux. (L) Rack	STD/QC/BLANK	11	10
2	Sample (13mm)	Samples	32	1
3	Sample (13mm)	Samples	75	1
4	Sample (13mm)	Samples	75	1
5	Sample (13mm)	Samples	75	1

--- Sample Sets ---

Set#	Type	Prepare?	Description	Method	#Pos	Rack#	StartPos
1	,Y	No	UMC09,UMC11 RE-AS,TL	UMASOIL	43	2	1

--- Preparation Info ---

Report As, Tl
KP 4/10/96

Set#	Uptake	Uptake#2	Final	Dil.Factor

No Samples Prepared.

Rack #1

Pos	Row	Col	Sample Name	Set #	#Used	Type
1	1	1	ICV1 MG4-48-01	-NA-	1	QC Standard
2	1	2	STD4 MG4-48-01	-NA-	1	Standard
3	1	3	STD3 MG4-48-01 5mls/10mls	-NA-	1	Standard
4	1	4	STD2 MG4-48-01 1ml/10mls	-NA-	1	Standard
5	1	5	STD1 MG4-45-02	-NA-	1	Standard
6	1	6	STD0	-NA-	1	Standard
7	1	7	Blank	-NA-	7	Blank
8	1	8	CCV MG4-51-01	-NA-	6	QC Standard

(9...19 Not Used)

Rack #2

Pos	Row	Col	Sample Name	Set #	#Used	Type
1	1	1	CRI11 MG4-45-02	1	-NA-	Sample
2	1	2	ICSABI1 MG4-52-05	1	-NA-	Sample
3	1	3	PBS1	1	-NA-	Sample
4	1	4	LCSS1	1	-NA-	Sample
5	1	5	03040-01	1	-NA-	Sample
6	1	6	03040-01D	1	-NA-	Sample
7	1	7	03040-01S	1	-NA-	Sample
8	1	8	03040-01L	1	-NA-	Sample
9	1	9	03040-02	1	-NA-	Sample
10	1	10	03040-03	1	-NA-	Sample
11	1	11	03040-01 5X	1	-NA-	Sample
12	1	12	03040-01D 5X	1	-NA-	Sample
13	1	13	03040-01S 5X	1	-NA-	Sample

LAUCKS TESTING LABORATORIES
ABN GC/MS OPERATIONS LOG

CASE # _____

PAGE 4883 -A

3/18/96 IS = MS334-1 DFTPP = MS334-4

RUN #	FILE NAME	CLIENT NAME	CLIENT SAMPLE#	LAB I.D. #	INJECTION INFO	IS A RT	IS A RESPONSE	IS B RT	IS B RESPONSE	IS C RT	IS C RESPONSE
1	MH7501										
2	HC18A	—	SSTD050	MS4-9-1	25.% ABN	11.24	55075	14.99	159300	20.44	104485
3	HC18B	—	SSTD200	MS3-89-1	100.% ABN/phenol	11.22	59100	14.98	168403	20.42	100469
4	HC180	Kalama	B0313961SVWLA	9603368-BLK	1000→1	11.23	58139	14.98	166207	20.43	99304
5	HC181	Kalama	S0313961SVWLA	—SPK	1000→1	11.24	55723	14.99	155289	20.44	98643
6	HC182	Olympia	—	9603206-01DL	1:4 1000→1	11.24	52364	14.98	158592	20.44	102071
7	HC183	Kalama	—	9603368-01	1:2 100→1	11.24	56997	14.98	168568	20.46	103091
8	HC184	↓	—	-01DL	1:4 100→1	11.24	58386	14.98	173180	20.45	106213

3/19/96

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1017

Title: Internal Audit Procedures

Revision history:

Number	Date
000	5/13/93
001	3/3/96

Written by: Harry Romberg Date: 3/3/96
Harry Romberg

Approved by: Karen T. Kotz Date: 3/3/96
Karen T. Kotz, Laboratory Director

UNCONTROLLED

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1. Introduction and Scope

1.1. Method Description

1.1.1. The purpose of this procedure is to provide instructions for planning, performing and reporting QA/QC audits within the laboratory.

1.1.2. This method is restricted to use by, or under the supervision of personnel experienced in the technique described.

1.2. Discussion

An Audit of the facility is performed for the following reasons:

1.2.1 To determine that contractual and regulatory obligations are fulfilled.

1.2.2 To determine that procedures and standards are being followed, and to insure good laboratory practice. These audits will include, but are not limited to the refrigeration unit temperatures, logbooks, balance calibrations, data, and standards traceability.

1.2.3 To establish that quality assurance objectives are met, including holding times, use of approved analytical methods, and stated objectives for precision and accuracy.

1.2.4 To serve as a management tool to evaluate appropriateness of quality assurance policies.

1.2.5 To identify potential or actual deficiencies for the purposes of evaluating compliance with requirements and providing the means for correction.

1.2.6 To determine that records are prepared and maintained as required.

1.3 Documentation and Frequency

Documentation required is specified in the text and the frequency shall be as required by the QA Manager, but at least one technical audit shall be performed annually for each department. This audit may take place in parts, with additional and more extensive audits being scheduled as deemed necessary.

1.4. Definition of Terms

1.4.3 This section defines terms and acronyms as they are used in this SOP.

1.4.4 SOP: Standard Operating Procedure

1.4.5 QA: Quality Assurance

1.4.6 QC: Quality Control

1.4.7 Audit: A planned and documented activity performed to determine by investigation, examination, or evaluation of objective evidence the adequacy of and compliance with established procedure, instruction, and other applicable documents and the effectiveness of implementation. An audit should not be confused with surveillance or inspection activities performed for the sole purpose of process control or product acceptance.

1.4.8 Auditor: Any individual: who performs or assists in the performance of any part of an audit, including technical specialists.

1.4.9 Lead Auditor: An individual who is qualified to organize and direct an audit, report audit findings, and evaluate proposed corrective actions.

1.4.10 Finding: Departure from approved procedures, program requirements, or other applicable documents that have, or in the immediate future could reasonably be expected to have, an adverse effect on the adequacy or effective implementation of the Laucks QA program. This would be ranked as a **critical** discrepancy in the audit report.

1.4.11 Deficiency: Departure from approved procedures, program requirements, other applicable documents, or good management practices that, if not corrected in a timely manner, could reasonably be expected to have a future adverse effect on the adequacy or effective implementation of the Laucks QA program. This would be ranked as a **minor** discrepancy in the audit report.

1.4.12 Discrepancy: Departure from approved procedures, program requirement, or other applicable documents that have, or may have an adverse effect on the adequacy or effective implementation of the Laucks QA program. This includes findings and deficiencies found during the course of an audit.

1.4.13 Recommendation: An observation or advise given to enhance current practices by any individual or department of the Laucks QA program. This would be ranked as a **recommended** item in the audit report.

2. Responsibilities

2.1 It is the responsibility of QA personnel, the auditor and audit leader to perform an audit according to this SOP and complete all documentation required for review.

2.1.1 QA Manager is responsible for the following:

- Approving each detailed audit plan
- Concurring with the adequacy of each audit report
- Issuing the audit report
- Tracking audit status through final closeout

2.1.2 If an audit team is used, the following responsibilities fall upon the Audit Team Leader. If an audit team is not used, the following responsibilities fall to the QA Manager:

- Developing the detailed audit plan
- Conducting pre-audit and post-audit conferences
- Supervising the conduct of the audit
- Preparing and signing the audit report

2.1.3 Management of audited departments is responsible for the following:

- Providing reasonable and timely access to personnel, facilities, and records, as required to support the audit process
- Providing timely and adequate response to audit reports, including determination and implementation of corrective actions, as required.
- Verifying initial implementation of corrective action for deficiencies in their areas, if applicable.

2.2 Audits and reports are to be performed by personnel in the laboratory who have demonstrated the ability to evaluate processes in the laboratory with emphasis on Quality Control and Quality Assurance.

2.3 Final review and sign-off of each Audit Finding Report may be performed by either the QA Manager. Lab Director or department supervisor or designee.

3. Safety precautions

3.1. Safety Precautions

3.1.1. Auditors must adhere to the general laboratory health and safety policies during the course of the audit.

3.1.2 Protective eyewear must be worn in all applicable locations at all times during the course of the audit.

4. Calibration and Quality Control

Not applicable.

5. Operation procedures

5.1 General

5.1.1 Audit personnel may be selected and assigned audit responsibilities commensurate with their training and expertise and the special nature of the activities to be audited.

5.1.2 Audit personnel are independent of any direct responsibility for performance of any activity which they will audit. Persons having direct responsibility for performance of the activities are not involved in the selection of an audit team.

5.1.3 Audit team members shall have received appropriate indoctrination and training for auditing.

5.2 Audit Planning

5.2.1 The QA Manager. or designee shall develop an audit plan which shall be the basis for the audit. The audit plan is documented on Audit Plan Form (Se Appendix I).

5.2.2 The QA Manager shall develop an audit checklist appropriate to the activity or area being audited. The checklist should contain auditable requirements extracted from the QA Manual,

applicable SOP's or guidance documents, such as EPA SW846. Checklists are designed for each Department by the QA Manager and can be accessed by the QA Department.

5.2.3 The QA Manager shall ensure that the checklist provides an adequate means for indicating whether the question is satisfactorily answered.

5.2.4 Audits are scheduled in a manner to provide coverage and coordination with ongoing QA program activities.

5.2.5 Audits are scheduled at a frequency commensurate with the status and importance of the activity. Within the audit program, each department of the laboratory and each element of the Laucks-QA program is audited, at a minimum, at least once annually.

5.2.6 The QA Manager notifies the audited department, in writing, prior to the audit to provide the subject and scope of the audit, audit schedule, and audit team members, if applicable.

5.3 Audit Performance

5.3.1 The QA Manager and (when required) the appointed audit team members shall proceed through the audit checklist recording evidence of compliance, discrepancies, or recommendations.

5.3.2 During the audit, the QA Manager or appointed team member shall use their best judgment to determine if there is a need to audit at a greater depth than the checklist indicates. If this is the case, the checklist shall be modified accordingly.

5.3.4 Objective evidence is examined, and essential information is recorded, such as the identification of specific evidence examined, specific details of discrepancies or adverse conditions, and applicable references.

5.3.5 The QA Manager shall identify each finding, deficiency, or recommendation in a QA audit report. Findings, deficiencies and recommendations will be listed by department and sequentially numbered in the QA audit report.

5.4 Audit Report

5.4.1 The QA Manager or his designee shall prepare an audit report which should address the following:

5.4.1.1 Date and location (Laucks-department) of the audit.

5.4.1.2 Purpose and scope of the audit.

5.4.1.3 Audit team members (when applicable) and the people contacted during the audit.

5.4.1.4 Description of items, including the rank, type and detail of the audit finding requiring corrective action. The description of the items must be in sufficient detail to enable investigation, evaluation, and correction of the finding. (See Appendix II - Audit Finding Report Form) The report may also include the area affected (See Table in Appendix III) and Finding Type (See Table in Appendix IV)

5.4.1.5 Due date for completion of corrective action plans.

5.4.2 The QA Manager shall issue the audit report to the appropriate levels of Laucks management within four following the audit. This report shall include a copy of each finding, deficiency and/or recommendation.

5.5 Audit Closure and Follow-Up

5.5.1 The appropriate Laucks Management (departmental supervisors, laboratory director hall investigate the reported finding, deficiency or recommendation and do the following:

5.5.1.1 Determine the actions required to correct the discrepancy.

5.5.1.2 Evaluate each discrepancy to determine the root cause of the problem and any generic implications.

5.5.1.3 Determine the corrective action required to correct the discrepancy and to prevent recurrence.

5.5.1.4 Document corrective action and indicate corrective action commitment date.

5.5.1.5 Sign, date, and return the completed form to the QA Manager within the assigned time frame given in the audit report.

5.5.2 The QA Manager shall evaluate each discrepancy/recommendation response. Inadequate or indeterminate responses shall be returned for reexamination of the problem and revised corrective action.

5.5.3 The QA Manager shall verify the corrective action, as stated in the response, and make sure it has been implemented and accomplished as scheduled.

5.5.4 An interim status report of corrective action completion may be issued

5.5.5 After verification of corrective action. the QA Manager shall issue a report stating that all corrective action has been completed and the audit is closed.

5.5.6 If a stalemate is reached concerning either the validity or resolution of an audit finding, affected personnel escalate the concern to the appropriate level of management to effect a resolution.

5.6 Records

The QA Manager shall ensure that the following audit documentation is maintained on file:

5.6.1 Completed audit checklist.

5.6.2 Audit Report (includes findings. deficiencies and recommendations).

5.6.3 Corrective Action (response to discrepancies).

5.6.4 Records pertaining to the completion of corrective action.

5.7 Audit Discrepancy Tracking

5.7.1 Audit discrepancies will be categorized to facilitate tracking and trending of recurrent problems. The categories are as follows:

- Logbook Maintenance
- Document Control Procedures
- QC Procedures
- Standard Operating/Quality Assurance Procedure
- Analytical Method
- Purchasing/Procurement Document Control
- Standards Preparation/Documentation
- Safety/Reagent Labeling or Storage

- Training/Records
- Good Laboratory Practices
- Other

5.7.2 Explanations of Categories Listed Above

5.7.2.1 Logbook maintenance findings include but are not limited to the following: logbooks not being maintained in accordance with Laucks policy, improper entries into logbooks, improper error corrections, logbooks not being kept up to date.

5.7.2.2 Document Control Procedure findings include but are not limited to the following: documents being maintained in such a way that is non-complaint with Laucks document control procedures (this includes archives, SOPs, QAPs, Chemical Hygiene Plan, HTVRs, and forms), records being stored in work areas for longer than 6 months, improper handling of controlled procedures.

5.7.2.3 QC procedure finding include but are not limited to the following: temperatures of ovens and refrigeration units not being monitored in accordance with procedures, balances and pipettes not being verified as required.

5.7.2.4 Standard Operating Procedure and Quality Assurance procedure findings include any case where a procedure has not been followed in full and has not been documented on the applicable corrective action from.

5.7.2.5 Analytical methods findings involve cases where the approved and required analytical method has not been followed to the full extent and there is no documentation that communicates this.

5.7.2.6 Purchasing and procurement document control findings involve instances where the appropriate procedures have not been followed in full. This type of finding includes but is not limited to the following: un-approved use of standards or solvents, lack of certification documentation, etc.

5.7.2.7 Findings for standards preparation and standards documentation include but are not limited to the following circumstances: improperly prepared standards, improperly documented standard preparation, inadequate verification documentation, lack of documentation when procedures are not followed in full.

5.7.2.8 Safety and reagent/chemical labeling findings involve any deviation from approved safety and waste procedures and the chemical hygiene plan.

5.7.2.9 Training and training records findings involve lack of training records, and personnel performing analysis without appropriate qualification documentation.

5.7.2.10 Good Laboratory Practice findings involve significant figures, temperature monitoring, calibration techniques and other associated activities involved with safe and accurate laboratory practices.

6.1 References

Laucks Quality Assurance Plan

Applicable SOPs

Audit Database Tables

Appendix I

Audit Plan Form

LAUCKS Testing Laboratories

Audit Plan

Area to be Audited: _____

Lead Auditor: _____

Audit Team Members (if applicable): _____
_____

Date of Audit: _____

Type of Audit: _____

Checklist(s) to be Used: _____
_____
_____
_____

Individuals Contacted During the Audit: _____
_____
_____
_____

Audit Debrief Date: _____

Report Issued Date: _____

Signature of Lead Auditor: _____

Signature(s) of Team Members: _____
_____
_____

Appendix II

Audit Finding Report Form

Audit Finding Report

Audit Number: Example	Finding Number 1
Facility:	Audit Date:
Auditing Body:	Audit Type:
Lead Auditor:	Affected Area: GC-Semivolatiles

Related Findings:

Finding Rank: Minor Repeat Finding?: No

Finding:

Corrective Action Response:

Opened By:	Date Opened:
Response By:	Response Date:
Corrective Action By:	Scheduled Completion Date:
Verified By:	Date Verified:

Appendix III

Area Names

Depart	Department	DepartmentDescription	Sup ID #
ARCH	Archive	Archive of Documents in QA	0006
BP	Bottle Prep	Bottle Prep	0008
DM	Data Management	Data Management and Administrati	0008
EXT	Extractions	Extractions	0027
GCEF	GC-Extractable Fuels	Extractable Fuels by GC/FID	0038
GCS	GC-Semivolatiles	GC-Semivolatiles	0048
GCV	GC-Volatiles	GC-Volatiles	0038
MSS	GC/MS-Semivolatiles	GCMS-Semivolatile	0048
MSB	GC/MS-Semivolatiles & Volatile	GC/MS-Semivolatiles and Volatiles	
MSV	GC/MS-Volatiles	GCMS-Volatile	0038
SAF	Health and Safety	Health and Safety	0006
HPL	HPLC	HPLC	0038
IN	Inorganics	Metals and Wet Chemistry Office	0053
MIS	LIMS and MIS	LIMs and MIS	0070
MET	Metals	Metals and Metals Prep	0067
MTI	Metals Instrumentation	Metals Instrumentation	0067
MTP	Metals Preparation	Metals Preparation	0067
PM	Project Management	Project Management	0008
QA	Quality Assurance	Quality Assurance	0006
SM	Sales and Marketing	Sales Department	
SC	Sample Control	Sample Control	0008
SP	Special Chemistry	Special Chemistry	0053
WC	Wet Chemistry	Wet Chemistry	0053
YAK	Yakima Office	Yakima Office	0072

Appendix IV

Finding Type

ID of Finding Type	Finding Type
BA1	Balance - Not Certified Annually
BA2	Balance - Not Checked Daily With Class S Weights or as used
BA3	Balance - Weights Not Certified Annually
BA4	Balances - Weights used for calibration do not correspond to weights used for analysis
CA1	Corrective Action - Procedures Not Developed
CA2	Corrective Action - NVC Not Being Tracked
DL1	Documentation/Logbooks - Error and Corrections not be documented correctly
DL2	Documentation/Logbooks - incomplete columns, not properly bound
DL3	Documentation/Logbooks - Not Maintained or used
DL4	Documentation/Logbooks - Inadequate Review
DR1	Data Review - Not Being Performed
DR2	Data Review - Not Being Documented
DR3	Data Review - No SOP
DR4	Data Review - No QC Decision Matrix Available
EC1	Electronic Backup - Not Being Performed
EC2	Electronic Backup - Not Inventoried For Retrieval
GL1	Good lab practice - misc GLPitems
MD1	Methods - No SOP/cribsheet available at time of audit
MD2	Methods - SOP/Cribsheet in use not current controlled version
MD3	Method- controlled SOP/Cribsheet is not being followed or doesn't match current practice
MD4	Methods - The controlled SOP is Non-compliant with the referenced published method
MD5	Methods - SOP/Crib sheets in use & not controlled, meaning draft or handwritten SOPs in use
PE1	Performance Evaluation Samples - Results are outside warning limits, check for error
PE2	Performance Evaluation Samples - Results are outside control limits, not acceptable
PE3	Performance Evaluation Samples - Results included misidentified compounds, not acceptable
QA1	QA - QAP/SOP Document Control Not in Place or Used
QA2	QA - Precision and Accuracy Data Not Current
QA3	QA - MDL/IDL Not Current
QA4	QA - QC Limits Not Determined or Maintained
QA5	QA - Control Charts Not Developed or Maintained
QP1	QAPlan - No QAP Available
QP2	QAPlan - Outdated And Needs Revision
QP3	QAPlan - Has Major Discrepancies With SOPs or practices of the day
RC1	Records Control - Logbooks Not Controlled
RC2	Records Control - Filing not maintained per SOP
RC3	Records Control - No SOPs to desribe System
RC4	Records Control - Not mentioned in QAP
RC5	Records Control - Archiving inadequate
SC1	Sample Control - Building not secured
SC2	Sample Control - COC not established or maintained per client requirements
SC3	Sample Control - Temp/pH not monitored for all regulatory samples
SF1	Safety - No SOP
SF2	Safety - Not Adhering to SOP or Chemical Hygiene Plan
SF3	Safety - Not Adhering to Good Lab Safety Practices
ST1	Stds/Reagents - No SOPs for preparation
ST2	Stds/Rgnts - Prep record inadeq./or not traceable
ST3	Stds/Reagents - Expiration Date Misused
ST4	Stds/Reagents - Not Labeled Properly in the laboratory
SW1	Software - Not Verified and Documented
TH1	Thermometer - NIST Not Available
TH2	Thermometer - NIST Not Evaluated Annually
TH3	Thermometers - Not Calibrated Annually
TH4	Thermometers - Correction Factor Not Applied or misapplied
TH5	Thermometers - Temp. Not Recorded Daily or As Used
TR1	Training - No Formal Program or Documentation
TR2	Training - Incomplete Forms (eg Proficiency, Hrs)
TR3	Training - Not Maintained Consistently

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1018

Title: **Overview of Review and Approval Practices for Validatable Data Packages**

Revision history:

Number	Date
0	06/17/96

Written by: Harry Romberg Date: 6-17-96
Harry Romberg, Quality Assurance Officer

Approved by: Karen J. Kotz Date: 6/20/96
Karen Kotz, Laboratory Director

UNCONTROLLED

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1. Introduction and Scope

1.1 Description

1.1.1 This SOP is intended to provide an overview and general organization of data review practices employed for validatable packages. The actual data review processes and check lists specific to those types of analyses are covered in specific SOPs. A schematic diagram of the general review process is provided in Appendix I.

1.1.2 Validatable packages are often similar to the Contract Laboratory Program (CLP) presentation, although the actual analyses themselves and the applicable quality control (QC) may be from SW 846 or other references. If such is the case, the CLP format would be modified to meet the requirements of the referenced methodology. However, the overall review process remains the same.

1.1.3 In-house (non-validatable) data packages receive much of the same review but do not necessarily follow the same process or the same level of documentation. It is not the intent of this SOP to outline the process for these data.

1.1.4 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described function.

2. Equipment List

2.1 Equipment

2.1.1 Data package or the portion of the data package to be validated

2.1.2 SOPs, including associated checklists, for the validation of the analyses of interest

2.1.3 Access to computer programs, etc. which may be required in order to complete the review process

3. Responsibilities

3.1 Analyst

3.1.1 It is the responsibility of the analyst to provide the first level of data review and to ensure that all criteria have been met or their failure addressed prior to releasing the data for the

next level of review. The analyst may only be the first level of review but is the most important in ensuring that the reported values reflect what was actually present in the samples. It is particularly important that the analyst be proactive in determining any actions that need to be taken in order that they may be completed within the holding time for that analysis and within the turnaround time required by the client.

- The analyst must ensure that the instrument was functioning properly at the time of analysis
- The analyst will ensure that all data comply with the method and project-specific requirements and that any deviations or failures to meet criteria are documented in the project file.
- The analyst must check to see that all calibration criteria were met
- The analyst must review all quality control data and ensure that criteria were either met or corrective action taken. This action may vary anywhere from simple narration in the report to re-analysis of the sample set, depending upon the QC failure and the method requirements.
- The analyst will review the final data to see that they make sense, that is, the values determined are reasonable, do not disagree with other information the analyst may be aware of, and that the calculated values appear to agree with the raw data.
- The analyst will either transcribe the data into the LIMS or will pass data to the person responsible for transcription in a format which can be easily interpreted.

3.2 Peer or Secondary Review

3.2.1 Data must receive a second level of review from a peer analyst. This analyst should be a person who is familiar with and capable of performing the analysis themselves. If there is no peer analyst available because the analyst in question is the only one experienced with the analysis or for other critical reasons, another qualified individual may substitute for the peer analyst. This person must still be familiar with all aspects of the calculations being performed and the relationships between data and performance of the method in order that the review can be properly conducted. The peer analyst reviewer must:

- Check 100% of the manual entries for transcription errors
- Check 100% of manual calculations for accuracy
- Spot check at least 10% of computer calculations to verify program validity
- Check for completeness of raw data or supporting materials
- Confirm spectral assignments and identification of TICs

- Check for appropriate use of significant figures and rounding
- Check reported values for dilutions
- Check for compliance with Method and project-specific requirements
- Check for reasonableness of data

3.3 Supervisor

3.3.1 The responsible supervisor or a designated alternate for the area in which the analysis is conducted must provide a technical review of the reported data. This level of review need not be as detailed as the peer review but must include:

- Checking for reasonableness and sensibility of the reported data
- Checking for completeness of the reported information
- Checking for compliance required QC practices including those specified in the Method and those that are project-specific.
- Checking for descriptions of deviations from Method and project-specific QC requirements
- Checking the information in the report narrative for sensibility

3.4 QA Review

3.4.1 QA cursorily reviews most data and periodically, in conducting data audits, reviews select packages more thoroughly. The cursory reviews are generally performed just prior to release of the data. In depth reviews almost always occur after release of the data and are intended more for a review and assessment of laboratory data and processes rather than an assurance of performance on that particular data package. Should quality issues arise that have a critical negative impact on the package being thoroughly reviewed, however, QA may call for more specific corrective action. QA may choose to go into any depth in review of data packages, but in general, most reviews will consist of:

- Checking for compliance with required QC practices
- Checking for reasonableness and sensibility of reported data
- Checking for deviations from Method or project QC requirements
- Checking for compliance with SOPs (periodically)

3.5 Project Manager

3.5.1 Project managers do not perform technical reviews but do review case narratives to ensure compliance with contractual agreements. Their responsibilities include:

- Reviewing to ensure that the client requested methodology was used and referenced
- Ensuring that sample entry comments were incorporated, and that concerns that were raised during the course of analysis which required client communication and decisions have been incorporated.
- Reviewing and signing project narratives.
- Reviewing the billing to ensure that the proper invoicing has occurred in conjunction with contractual agreement.

3.6 Management

3.6.1 Senior management reviews case narratives and other components of data packages, should they find cause. They are the parties responsible for approving the release (signing) of reports.

4. Operation Procedures

4.1 General

4.1.1 The processes described below are general. Specific QC and practices, including most of the corrective actions resulting from QC failures are generally described in the appropriate SOPs. The specifics of the review process for individual analyses are specified in the respective data review SOPs along with their associated checklists.

4.1.2 The duties of individuals responsible for various levels of review are specified in the Responsibilities section of this SOP. It is the responsibility of each reviewer to be familiar with this SOP and those specific to their function.

4.2 Analyst

4.2.1 The analyst must be cognizant of the entire analytical process and document anything out-of-the-ordinary that goes on during the analysis. This may include on-the-spot corrective action, such as dilution and re-analysis. The analyst must also review the data during the production of final results to ensure that all criteria are met and that all

appropriate commentary regarding the analysis and any extraordinary steps are clearly noted.

4.2.2 The analyst will then assemble the final data package according to the SOP and submit the data for review to the secondary reviewer. The work of the analyst is the most critical in the review process as this ensures the timely processing of the samples in order to meet holding and turnaround times.

4.2.3 When completed with the data package, the analyst will pass all of the associated materials along to the second reviewer.

4.3 Peer or Secondary Review

4.3.1 The secondary review will usually include use of the checklists associated with the data review SOPs. If in doubt, the secondary reviewer will ask the analyst for further information and not just pass along problems to the next level. In consultation with the supervisor or QA, data may be returned to the analyst for corrective action.

4.3.2 The secondary reviewer will pass the data and checklist along to the supervisor

4.4 Supervisor

4.4.1 The area supervisor or designate will perform the functions outlined under the Responsibilities section, paying special attention to data review checklist items which do not meet method specifications. The supervisor may determine that corrective actions are necessary in the pursuit of data of adequate quality or may consult with QA where the optimal practice is questionable. The supervisor should ensure that corrective actions are all completed and all report commentary is sound prior to submitting the data to the reports department.

4.5 Reporting

4.5.1 The reporting group assembles the respective data packages but bears no responsibility for review other than to ensure that all of the analyses are present in the package, that everyone has input their respective commentary into the report narrative, that all narrative comments have been printed and the appropriate parts of the data package have been assembled. This aspect is detailed in an SOP designed for that purpose.

4.6 Quality Assurance

4.6.1 QA performs cursory reviews of most narrative and data packages before release. QA may call for corrective action at any level should problems be observed which have not been dealt with in an appropriate manner prior to this late stage of reporting. Responsibility to spot and have errors corrected, however, must not be left up to QA if they are spotted earlier or the analysis and reporting of results will almost certainly be delayed.

4.6.2 QA will also perform a more thorough review of select data packages, the scope of which is at the discretion of QA and is not addressed in this SOP. Such review will be more detailed, however, and corrective actions may result which will impact the immediate data or, more likely, affect the processes involved in collecting, reviewing, or reporting data in general.

4.7 Project Management

4.7.1 Project managers review and sign project narratives. They will review only to ensure that the client requested methodology was used and referenced, that sample entry comments were incorporated, and that concerns that were raised during the course of analysis which required client communication and decisions have been incorporated. They must also review the billing to ensure that the proper invoicing has occurred in conjunction with contractual agreement. They may perform these tasks either before or after QA review.

4.8 Management

4.8.1 Management will review and release (sign) narratives.

5. Reports

5.1 Data Review and Signatures

5.1.1 Data review forms are provided in individual data review SOPs.

5.1.2 Analyst/reviewer signatures occur on organics cover pages. Inorganics review signatures occur on data cover pages and supervisor signatures are included on both metals and conventional chemistry packages.

5.1.3 Management signatures appear on all final reports.

6. References

Navy Installation Restoration Laboratory Quality Assurance Guide, Naval Facilities Engineering Service Center, February 1996

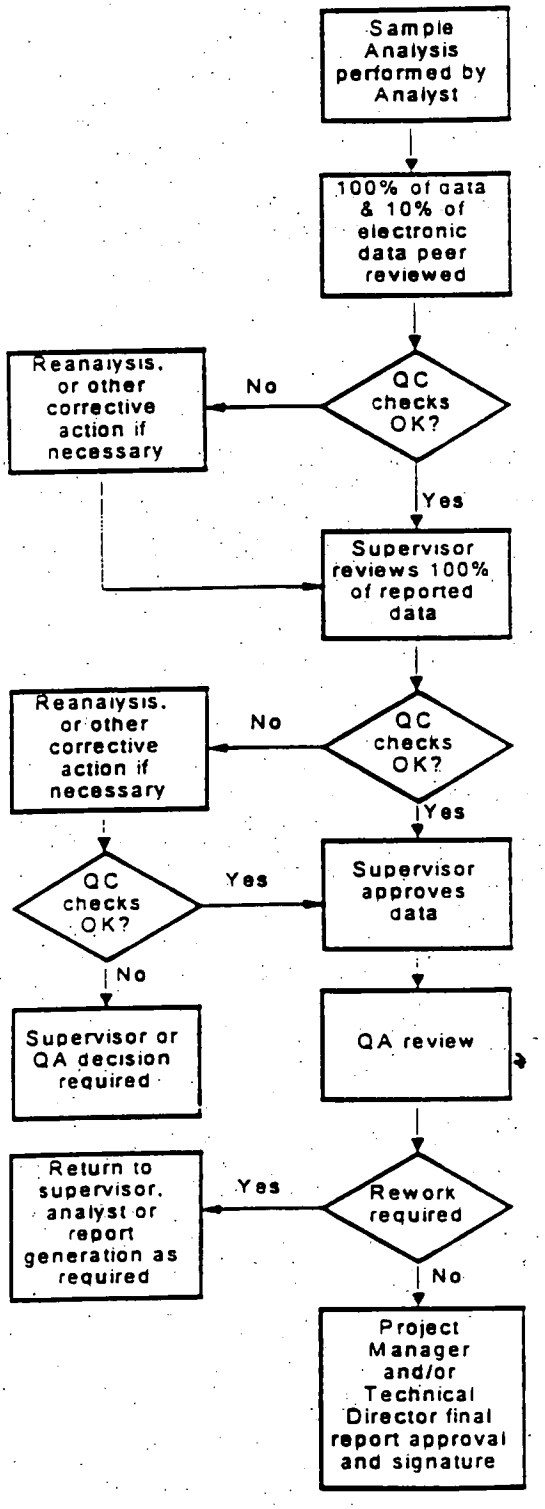
Laucks SOPs

LTL-7001	Metals Data Review
LTL-7002	EPA Inorganics Data Review
LTL-8001	GC Hydrocarbons Data Review
LTL-8002	GC Pesticides/PCBs Data Review
LTL-8003	GC Herbicides Data Review
LTL-8004	GC Volatiles Data Review
LTL-8005	GC Gas/BTEX Data Review
LTL-8201	GC/MS Volatiles Data Review
LTL-8202	GC/MS Semivolatiles Data Review
LTL-8301	HPLC Aromatics 8310 Data Review
LTL-8302	HPLC Ordnance 8330 Data Review
LTL-9001	Inorganic Conventionals Data Review

Appendix I

Data Review Schematic

Data Review and Approval



-100 % maniual entries for transcription errors
-100% of manual calculations for accuracy
-10% spot check of computer calculations
-Check for completeness of raw data or supporting materials
-Confirm spectral assignments and identification of TICs
-Check for appropriate use of significant figures and rounding
-Check for compliance with Method or Project QC requirements
-Check for descriptions of deviations from Method or Project QC requirements
-Check reported values for dilutions
-Check reasonableness of data

-Check for reasonableness of reported data
-Check for completeness of the reported information
-Check for compliance with required QC practices
-Check for descriptions of deviations from Method or Project QC requirements
-Check the information for the report narrative

-Check for compliance with required QC practices
-Check for reasonableness of reported data
-Check for descriptions of deviations from Method or Project QC requirements
-Check for compliance with approved SOPs (periodically)

P:\SOP\QA_SOPS\RVW_CHT1.QFC 6/13/96

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1019

Title: **Controlling, Maintaining, and Monitoring Laboratory Logbooks**

Revision history:

Number	Date
0	4/11/96
1	5/13/98

Written by: Harry Romberg, QA Officer Date: 5-13-98

Approved by: Kathy E Kreps, Laboratory Director Date: 5-18-98

Controlled Document

No. 20 Assigned to: Tetra

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EXAMPLE LOGBOOK REVIEW LABEL 11

1. Introduction and Scope

1.1 Scope

1.1.1 The maintenance of logbooks is essential to monitoring all aspects of laboratory operations including instrument and method performance and in tracking analyses. It is also important to confirming instrument performance at the time of specific analyses and in monitoring ongoing or periodic performance degradation and the steps taken to correct or prevent such occurrences. This document applies to all personnel involved in the preparation, control and use of laboratory notebooks.

1.1.2 More specific instructions for maintaining logbooks can be found in pertinent SOPs, such as LTL-1007 "Maintaining Instrument Records and Logbooks" or LTL-1005 "Analytical Balances" or others specific to other laboratory operations.

1.2 Purpose

1.2.1 The purpose of this SOP is to define the practices used to maintain control and use of laboratory logbooks. This SOP is not intended as a specific description of any particular logbook type but covers the practices that must be in place for all logbooks employed at Laucks.

1.3 Definition of Terms

1.3.1 Logbook - Any bound or unbound document that forms a record of activities and pertinent data regarding an activity including but not limited to maintenance logs, standards logs, reagent chemical logs, analysis logs including instrument outputs (computer generated or strip chart recordings), balance and temperature logs, or any other regularly maintained record of activity.

2. Requirements

2.1 Control

2.1.1 Documents that specify quality requirements or activities affecting quality or evidentiary activities shall be controlled to ensure that correct documents are being used and properly archived when completed.

2.2 Maintenance

2.2.1 Quality assurance records (logbooks) shall be compiled and maintained in accordance with approved procedures.

2.3 Monitoring

2.3.1 Logbooks should be periodically monitored to ensure they are being properly maintained and information is being correctly recorded. Standard logbooks and run logs should be monitored at least semiannually by group supervisors or their designees. Maintenance and other logbooks need only be reviewed annually, unless previous review has demonstrated inadequacies in the logbook which require more frequent monitoring.

3. Responsibilities

3.1 Quality Assurance Manager

- Maintain the logs for control of laboratory notebooks and provide control numbers and labels as required.
- Approve format and proposed content of laboratory notebooks; minor changes to pre-printed forms do not need QA approval as long as their basic content does not change.
- Maintain master copies of notebook pages (in instances where pre-printed pages with a specific format are used); this may be in electronic or hardcopy form or both.
- Monitor satisfactory implementation of the requirements of this SOP

3.2 Responsible Supervisor

- Determine the format and content of notebooks used in their respective areas.
- Ensure that QA has been provided with an electronic version of all pre-printed logbook pages in order that they are later available for reprinting or editing.
- Ensure that all laboratory notebooks are properly labeled, including the appropriate control number.
- Ensure that personnel are adequately trained in the proper use of laboratory notebooks
- Periodically review laboratory notebooks to verify satisfactory implementation of the requirements of this SOP. Standard logbooks and run logs should be monitored at least semiannually by group supervisors or their designees. Maintenance and other logbooks need only be reviewed annually, unless previous review has demonstrated inadequacies in the logbook which require more frequent monitoring. This activity may be assigned to another individual but should not be the same individual who regularly completes the log itself.

3.3 Analyst

- Ensure that they are using the appropriate logbook and understand how to properly fill in the required fields.
- Ensure that any new logbook has been given a logbook number by QA before beginning to use it.
- Ensure that the logbook is clearly identified with an instrument ID and purpose or other appropriate title which will enable the analyst to easily identify the logbook.
- Ensure that if pre-printed logbook pages need to be modified, the modifications are approved by their supervisor and that an electronic copy or, if requested an original hardcopy have been provided to QA.

4. Procedure

4.1 Notebook Structure

4.1.1 Laboratory notebooks may be either bound or unbound as described below. Most logbooks should be bound in some fashion but it is recognized that this is not always possible, such as for vendor service records. These records may be stored in 3-ring binders or other suitable notebooks.

4.1.2 In some instances, logbooks may be created from instrument printouts or other pages that do not lend themselves to being pre-bound. In these instances, the log sheets may be stored in a 3-ring binder or other storage until enough sheets have been accumulated to have them bound with the laboratory comb binder.

4.1.3 All logbooks whether bound or unbound must be controlled by QA as designated by the appropriate QA Book Number label (see example in Appendix 1).

4.1.4 Bound notebooks shall conform to the following:

- Where feasible, binding will be of a type that will make the removal and reinsertion of pages readily noticeable.
- If pre-printed and bound, all pages will be sequentially pre-numbered. If the format of the notebook permits the use of the reverse side of the pages, both sides of each page will contain a sequential page number.

- Each page of the pre-printed bound notebook will contain, as a minimum, the laboratory name, logbook title, and sequential page number. Other elements may also be necessary for any specific logbook.

4.1.5 Unbound notebooks shall conform to the following:

- Unbound pages will be contained in a binder or folder that provides protection from damage.
- Each unbound page will contain a unique identifier (e.g., run number/date). For identification purposes, a continuous printout on fanfold computer paper requires only one identifier unless the sheets are separated.
- As noted above in 4.1.2, some unbound logbooks may eventually be bound if practical.

4.1.6 All notebooks will contain the following information on the cover:

- Laboratory name, Laucks Testing Laboratories, Inc.
- Control number assigned by the Quality Assurance Officer
- The department to which the logbook was issued
- The use of the logbook (i.e. balance calibration. instrument run-log, etc.)
- The department book number or title uniquely identifying that book, as required to identify the specific use of the book. This may include an instrument number or other logbook ID (such as a standards logbook ID). This is in addition to the QA logbook number.
- Start Date, the date on which the first entry was made
- End date, the date on which the last entry was made

4.2 Control of Logbooks

4.2.1 The QA Officer will maintain a master log of laboratory notebooks that contains as a minimum, the following information:

- Unique control number for each logbook
- Logbook title, which should reflect the type of information to be entered.

- Department to whom issued, for accountability only. A logbook will generally be assigned to a work station or function, and in no way is a laboratory notebook to be considered a "personal" notebook.
- Date issued, for accountability only.
- Date closed, for accountability.

4.2.2 Master sheets for each logbook will be maintained by the QA Officer and will be utilized for producing notebooks when required.

4.3 Use of Laboratory Logbooks

4.3.1 The notebook is the basic document for recording information. Entries should be made into the notebook in real time, not written on scratch paper and transferred later.

4.3.2 Handwritten entries should be legible and entered in black or blue indelible ink.

4.3.3 Computer-generated data should be printed out and collected at appropriate times to represent the activities being recorded.

- Computer printouts may be either placed in unbound notebooks as described above, or inserted into bound notebooks.
- Computer printouts or other material inserted into bound notebooks must be securely fastened (tape is preferred) in such a way that removal and insertion of material can be determined readily.

4.3.4 When information from related activities is recorded in more than one notebook, provide adequate cross-reference information in all affected notebooks so that all pertinent data can be readily accessed.

4.3.5 Do not skip pages when entering data. For example, if data is not readily available for entry, do not leave space for later entry. Enter the data when it becomes available and provide adequate cross-references if required.

4.3.6 In cases where partial or complete pages must be left blank and not used, indicate the unused portion by placing a horizontal line at the beginning and end of the unused portion and connecting opposite ends of the horizontal lines with a diagonal, resulting in a Z-shaped figure. The individual striking out the blank area will initial and date the diagonal.

4.3.7 Errors or other changes must be deleted in a similar fashion or with a single-line cross-out which has been initialed and dated. **No erasures, overwriting, white-out or multiple-line cross-outs (blacking out) are acceptable.**

4.3.8 When pre-printed formats are used and all possible entries are not required, the remaining blanks may be struck out with a Z as described above, or entries such as N/A may be placed in the unused blanks.

4.3.9 The individual entering information into the notebook shall initial and date each page used, or in the case of logbooks with ongoing records which do not occupy the entire page, such as maintenance logs or balance logs, each individual entry.

4.4 Supervisory Monitoring of Laboratory Logbooks

4.4.1 Standard logbooks and run logs should be monitored at least semiannually by group supervisors or their designees. Maintenance and other logbooks need only be reviewed annually, unless previous review has demonstrated inadequacies in the logbook which require more frequent monitoring. This activity may be assigned to another individual but should not be the same individual who regularly completes the log itself.

4.4.2 Logbooks should be reviewed using the review items provided in Appendix II, although it is not necessary to actually document the review using this checklist.

4.4.3 Errors should be formally brought to the attention of the responsible individual through the use of Corrective Action Forms. If errors are correctable or items can be corrected for legibility problems, they should be corrected using the proper error correction technique.

4.4.4 Logbooks that have been reviewed are marked with a fluorescent yellow or other colorful label that looks similar to the label in Appendix III.

4.5 QA Monitoring of Laboratory Logbooks

4.5.1 The QA Officer will verify during periodic audit and surveillance activities that notebooks are properly completed and maintained. This will generally be done approximately annually as part of routine audits. This observation does not preclude the requirement for supervisory review.

Appendix I

Example QA Logbook Label

Laucks
Testing Laboratories, Inc.

QA Book No.: _____

Issued To: _____

Used For: _____

Dept. Book No.: _____

Start Date: _____

End Date: _____

Appendix II

Example Logbook Review Items to be Observed

- Have all pertinent fields been filled or marked not applicable (N/A)?
- Has empty space been crossed out properly initialed and dated?
- Have errors been corrected with single-line crossouts, initialed and dated (no obliterations or overwrites)?
- Are all entries clear and easy to read and comprehend?
- If calculations are involved, check several random calculations for error.
- If traceability is involved (as for standards) check several random entries to confirm that the logbook entries can be tracked back to the original entry.
- If standards log, observe some actual standards and compare them against logbook entries for accuracy.
- Are all handwritten entries initialed and dated?
- If the book is beginning to deteriorate, it should be repaired or retired and replaced.

Appendix III

Example Logbook Review Label

Logbook pages _____through_____
have been reviewed for completeness and
spot-checked for accuracy>

Initials:_____ Date:_____

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-1020

Title: **The Integration of IC, GC, HPLC, and GC/MS Peaks**

Revision history:

Number	Date
0	08/26/96
1	08/21/97

Revised by: _____ Date: 8/25/97
Monica Carr, Organics Division Manger

Reviewed by: _____ Date: 8-25-97
Harry Romberg, QA Officer

Approved by: _____ Date: 8/25/97
Karen Kotz, Laboratory Director

UNCONTROLLED

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1. Introduction and Scope

1.1 Method Description

1.1.1 This SOP describes the integration process for chromatographic data, the procedures for manual integration, and the procedures for documenting manual integration.

1.1.2 Integration identifies peaks found in the data collected during data acquisition and characterizes them. The software uses the integrated peaks to determine the identity and quantity of compounds in the samples. The peak area, peak height, peak type, baseline, and retention time of each peak in a chromatogram are determined by integration. Some peaks, due to limitations of the software, will need to be manually integrated. The manual integration process must be documented. This documentation will include a brief description of why it was necessary, who did it, when was it done, and a hardcopy of the re-integrated peak.

1.1.3 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Definition of Terms

1.2.1 Manual Integration - any intervention by an analyst or supervisor to change the peak area, peak height, baseline, peak type, or retention time of a chromatographic peak.

2. Software

2.1.1 GC Acquisition-HP/LAS and EZChrom
2.1.2 GC/MS-Teknivent/EnviroQuant
2.1.3 GC-Target

3. Responsibilities

3.1 Analyst

3.1.1 The analyst is responsible for reading and understanding this SOP and that which is applicable to the method of analysis. The analyst must also perform and document all manual integrations as specified in this SOP.

3.2 Supervisor

3.2.1 The supervisor or designated data reviewer must verify that all manual integrations are performed according to this SOP. The supervisor or designated data reviewer must document that this verification has occurred per the applicable Data Review, Validation, and Reporting SOP.

4. Operation Procedures

4.1 Integrator operation

4.1.1 The ideal chromatogram has perfectly symmetric peaks separated from each other with periodic baseline points. It is common to encounter split peaks, deformed peaks, merged peaks, sloping baselines, noise, spikes, shoulders on peaks, and a host of other calamities.

4.1.2 To maximize the chances of obtaining ideal chromatograms: optimize the chromatography.

4.1.3 Peak recognition and integration sequence - As the integrator scans the data, it examines the slope (vertical distance between points) and curvature (positive or negative). So long as these remain within preset bounds data is interpreted as the baseline. If the bounds are exceeded, a peak may be starting. If the condition persists, the integrator decides that it is on the upslope of a peak.

4.1.4 The curvature changes to negative about halfway up the peak. This is the inflection point where the peak starts to round over approaching the apex. Passing the top, the slope becomes negative and the integrator is on the downslope. Another inflection point comes on the downslope and finally the peak returns to the baseline (Figure 1).

4.1.5 Finite width of integration slices - The slope changes from positive to negative at the top of the peak. However for area slices having finite width the integrator can only determine which slice contains the peak apex. To get better values for the retention time and peak height, the integrator takes the slice containing the-apex and one slice on either side, fits them to a quadratic equation, and solves the equation to find the highest point (Figure 2).

4.1.6 Optimizing peak recognition - The best conditions for recognizing isolated symmetric peaks on a quiet baseline is to match the peak width parameter to the measured width of the peaks at half height. Threshold should be a few units less than the highest value still capable of detecting the peak. When peaks cluster together or the baseline slopes or is noisy, these ideal values must be modified. Figure 3 shows the effects of changing the values.

4.1.7 Manual integration - It is important that the analyst is familiar with the compounds that are routinely analyzed. Knowing the response and peak shape of the standard is important for consistency in integration. It is best to optimize the method to process data so that manual intervention is minimized and peak integration is more consistent. If manual integration is performed, it is important to be consistent for a given analyte in the standards, blanks, spikes, and samples.

4.1.8 Allowable manual integrations - Some common reasons for manual integration are:

4.1.8.1 Split peaks (attachment 1)

4.1.8.2 Tailing (attachment 2)

4.1.8.3 Retention time shifts (attachment 3)

4.1.8.4 Mis-identification (attachment 3)

4.1.8.5 Merged peaks (attachment 3)

4.1.8.6 Secondary ions or qualifier ions (attachment 4)

4.1.8.7 Baseline shifts (attachment 5)

4.1.8.8 Skimming versus dropped baseline (attachment 6)

4.1.9 Improper manual integrations - These practices are not allowed and warnings up to and including termination of employment will follow any documented cases of improper manual integration. If you are unsure about a manual integration ask your supervisor or QA.

4.1.9.1 Adding area by including other peaks. (attachment 7)

4.1.9.2 Improper baseline - this includes the practice of having the baseline moved up the side of a peak to decrease the area. (attachment 8)

4.1.9.3 Changing a proper integration to make the peak "in".

4.1.10 Special rules for fuel analyses (*e.g.*, gasoline, diesel) - The integration of these multi-component analytes requires special integration rules. The area of all peaks (with the exception of the surrogates) and the area of the non-resolved components (hump) are grouped together to determine the quantity of the analyte. The baseline is fixed at the start and held at a constant level for the entire run. When integration of the baseline for fuel analyses is performed, the

quantitation report will not be dated and initialed by the analyst. Instead an explanation of the baseline integration will be documented on the quantitation report or in the appropriate SOP and discussed in the sample narrative. Some acceptable multi-analyte integrations are shown in attachment 9.

5. Documentation

5.1.1 When any manual integration is performed , a graphic copy of the peak with the integration marks is generated and put into the folder with the chromatograms and quantitation reports for that sample. The three different software systems used in the laboratory are listed below with the commands for generating the copy. On the quantitation report the analyst must initial, date, and give a brief description of the reason for the manual integration (table 1). The manual integration must also be documented in the associated sample narrative. The supervisor will look at each manual integration during data review and complete the summary on the data review or QC checklist.

5.1.2 Target: After changing the integration, exit and save in Target Review.

5.1.3 GC/MS Teknivent EnviroQuant: After using Qedit to change the peak click on 'Graphics Report to Printer'

5.1.4 EZChrom: After changing the integration, toggle the "Reanalyze" key and print.

5.1.5 LAS - After changing the integration, print the chromatogram.

Table 1

Manual Integration Key

M = Manual integration due to missed peak or irregular peak shape.
MS = Manual integration due to split peak.
MR = Manual integration due to retention time shift.
MI = Manual integration of correct isomer.
MT = Manual integration due to peak tailing.
MB = Manual integration due to irregular baseline.

6. REFERENCES

6.1.1 Target Manual, Thru-Put Systems, Inc., Target Compound Analysis Software User's Guide, 1994.

6.1.2 Envirolink User's Manual, TEKNIVENT, 1994

6.1.3 EZChrom Chromatography Data System, Scientific Software, Rev. 6.6, 1995.

6.1.4 Wisconsin DNR Newsletter, October 1994.

6.1.5 - SOP# LTL-1018, Standard Operating Procedure for Review and Approval Practices for Validatable Packages.

6.1.6 SOP # LTL-8005, Standard Operating Procedure for GC Gas/BTEX Data Review.

6.1.7 SOP #LTL-8004, Standard Operating Procedure for GC Volatiles Data Review.

6.1.8 SOP #LTL-8001, Standard Operating Procedure for GC Hydrocarbons Data Review.

6.1.9 SOP #LTL-8301, Standard Operating Procedure for HPLC Aromatics 8310 Data Review.

6.1.10 SOP #LTL-8302, Standard Operating Procedure for HPLC Ordnance 8330 Data Review.

6.1.11 SOP #LTL-8201, Standard Operating Procedure for GC/MS VOA Data Review.

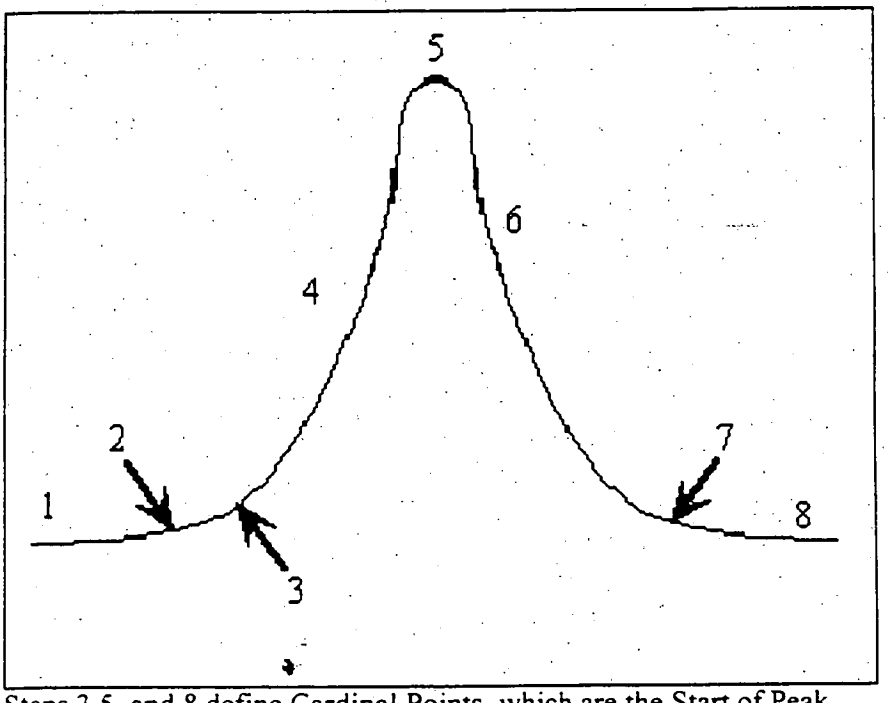
6.1.12 SOP #LTL-8202, Standard Operating Procedure for GC/MS Semivolatile Data Review.

Appendix I

Fig 1.

The sequence for finding a positive peak is:

1. Slope and curvature within limits	track baseline
2. Slope and curvature above limits	perhaps a peak?
3. Slope remains above limit	here's a peak!
4. Curvature becomes negative	front inflection point
5. Slope becomes negative	top of peak
6. Curvature becomes positive	rear inflection point
7. Slope and curvature within limits	approaching end of peak
8. Slope and curvature remain within limits	end peak, track baseline



Steps 3,5, and 8 define Cardinal Points, which are the Start of Peak, Apex, and End of Peak Respectively

Fig 2.

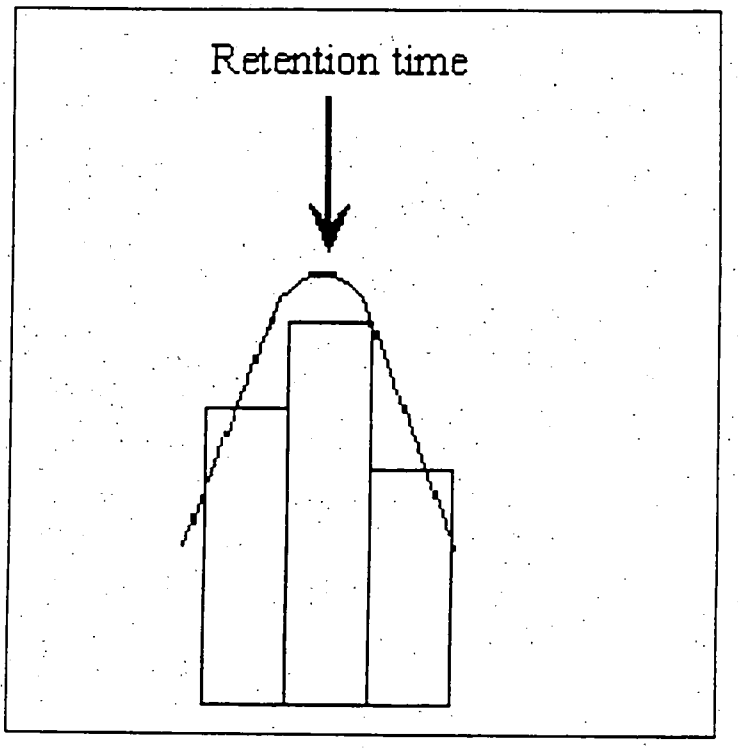
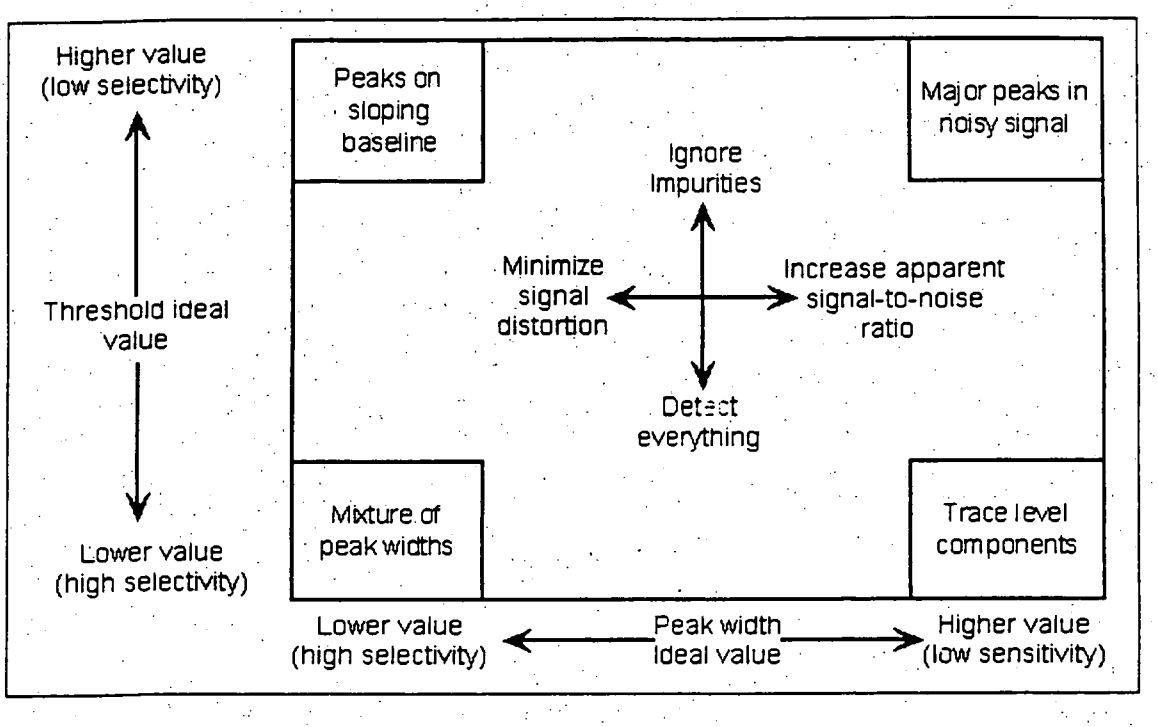
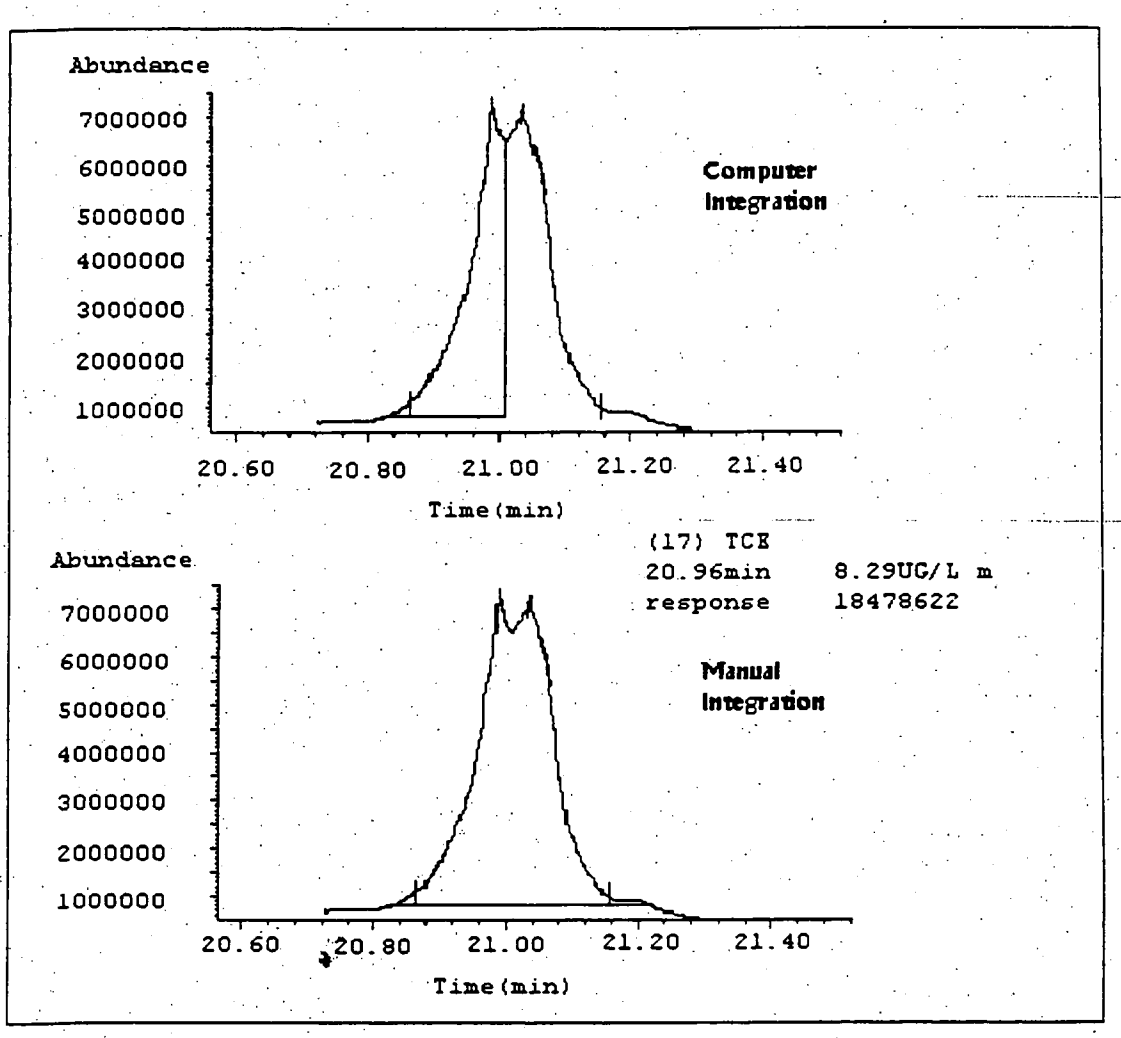


Fig 3.


Higher value
(low selectivity)
Threshold ideal
value
Lower value
(high selectivity)
Peaks on
sloping
baseline
Major peaks in
noisy signal
Ignore
Impurities
Minimize
signal
distortion
Increase apparent
signal-to-noise
ratio
Detect
everything
Mixture of
peak widths
Trace level
components
Lower value
(high selectivity)
Peak width
Ideal value
Higher value
(low sensitivity)

Appendix II

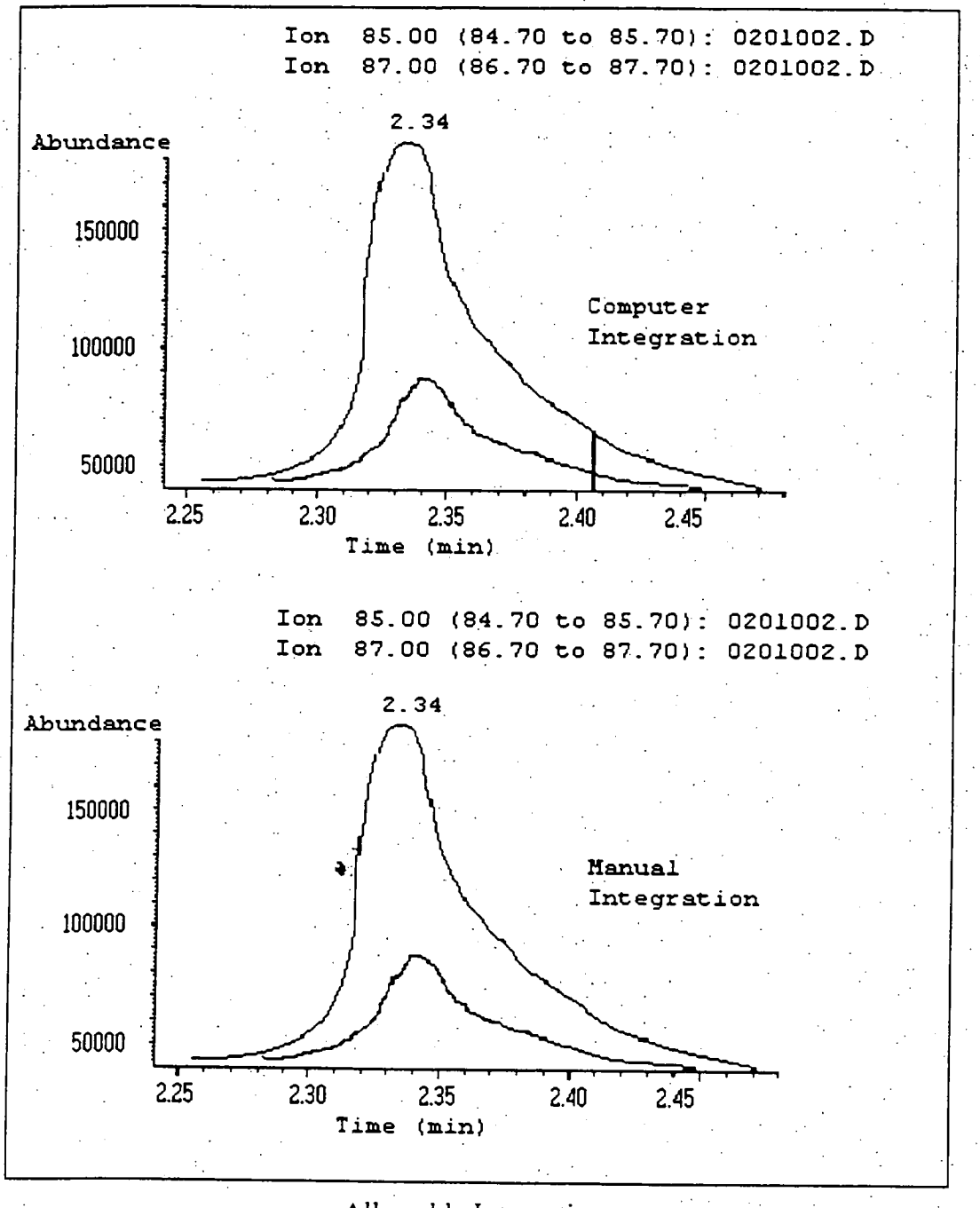
Attachment 1



Allowable Integration

Split Peaks

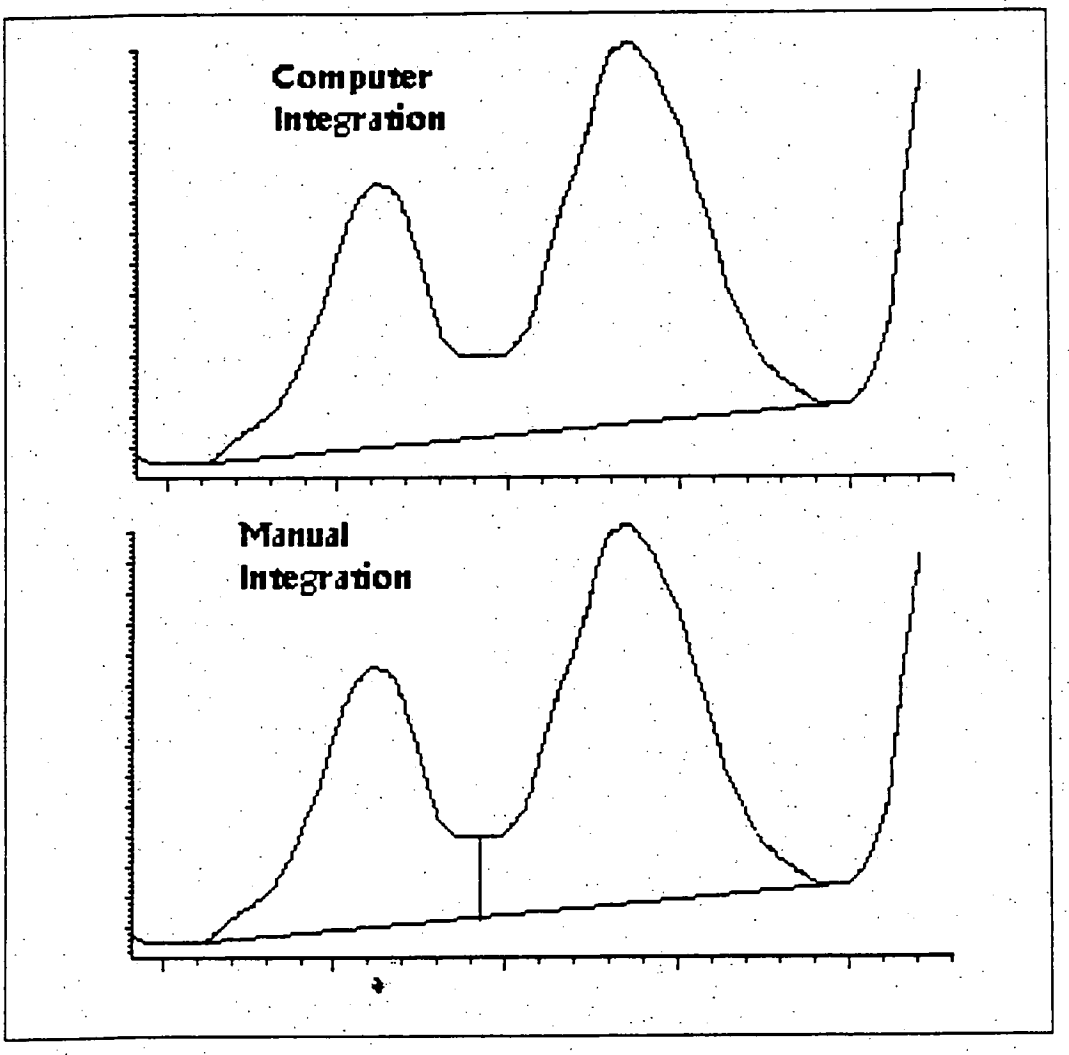
Attachment 2



Allowable Integration

Tailing

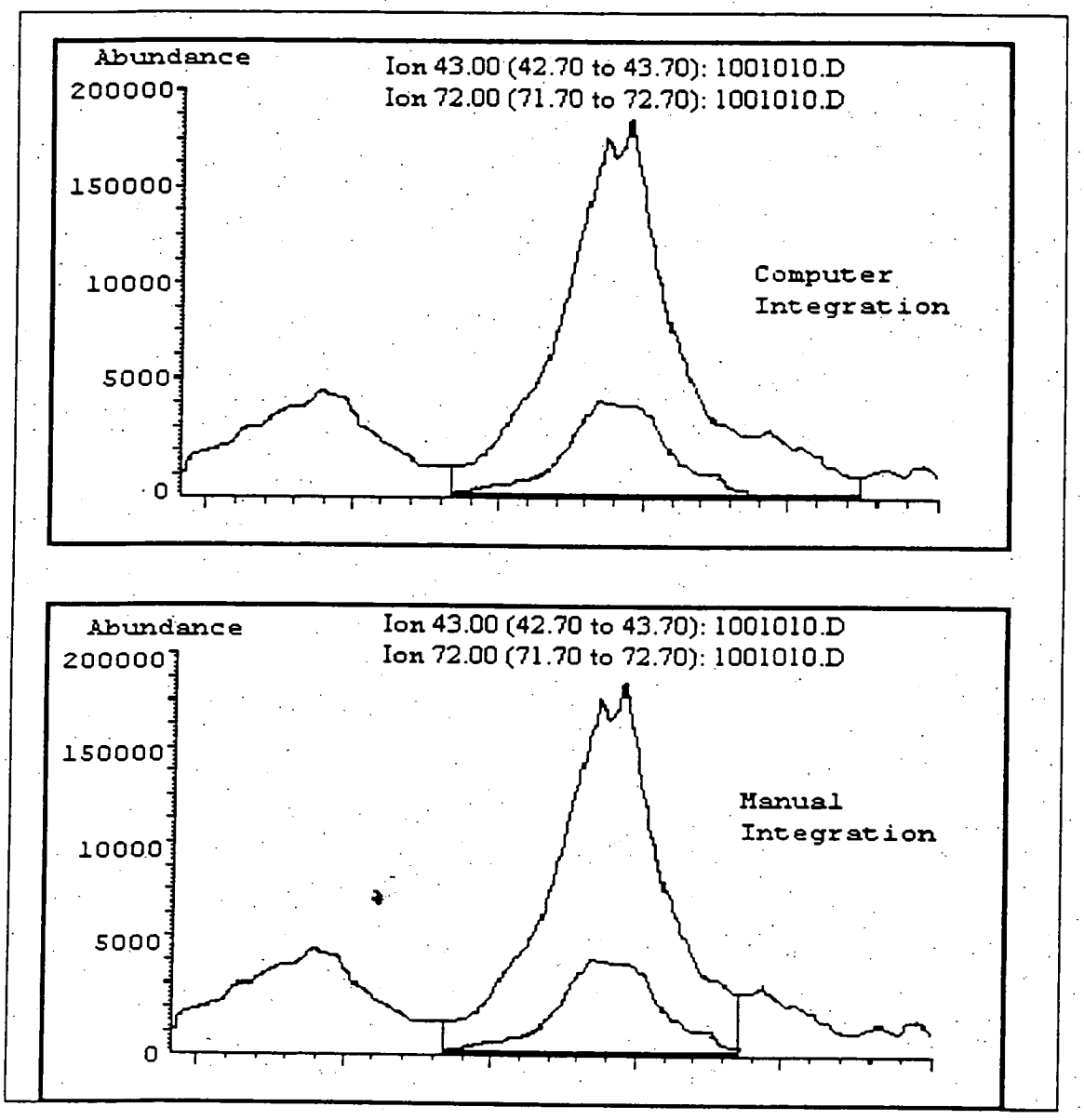
Attachment 3



Allowable Integration

Retention Time Shift - Mis-Identification - Merged

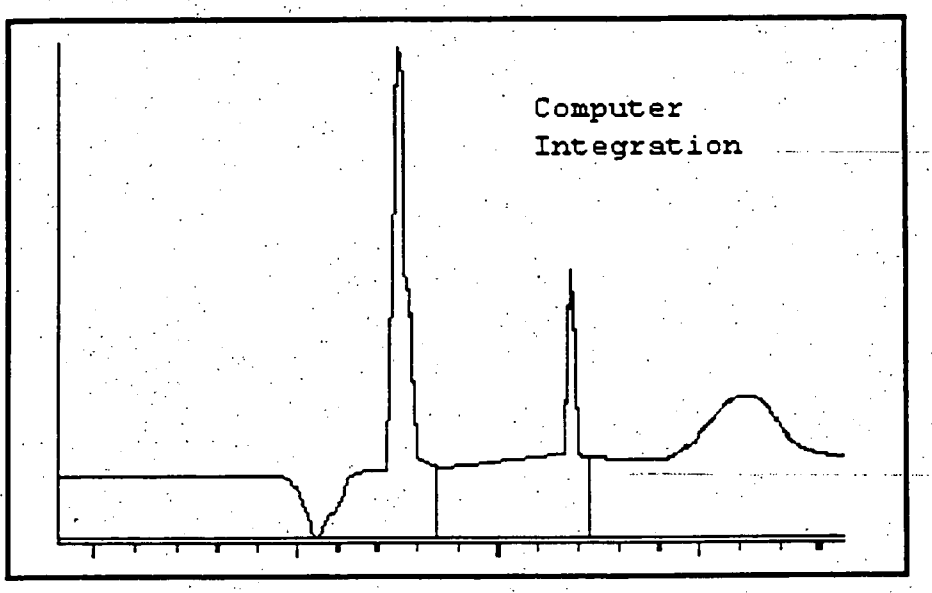
Attachment 4

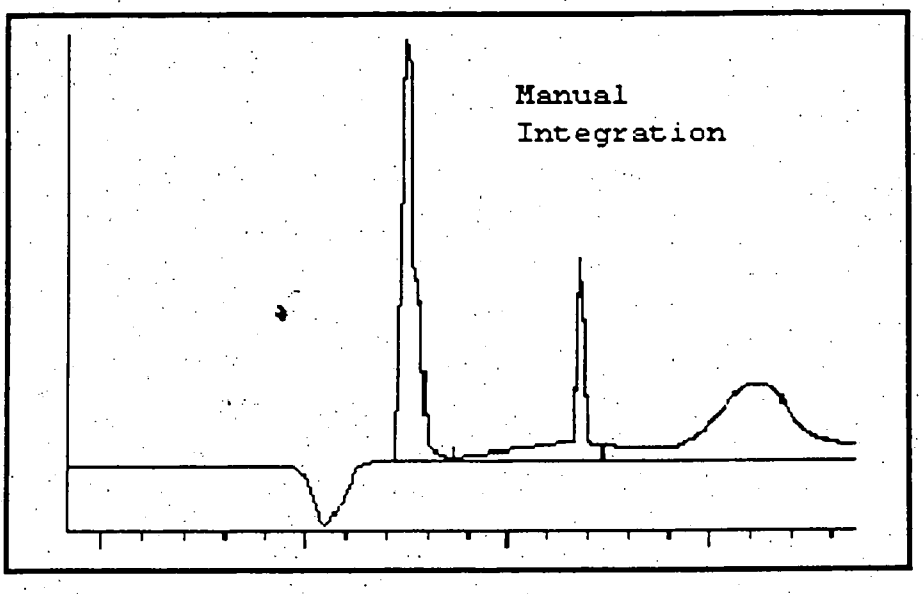


Allowable Integration

Secondary or Qualifier Ions

Attachment 5

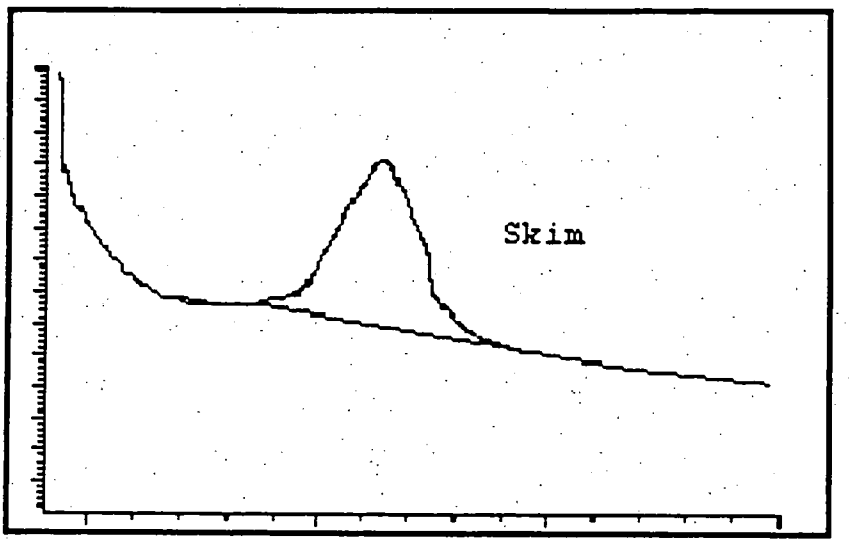


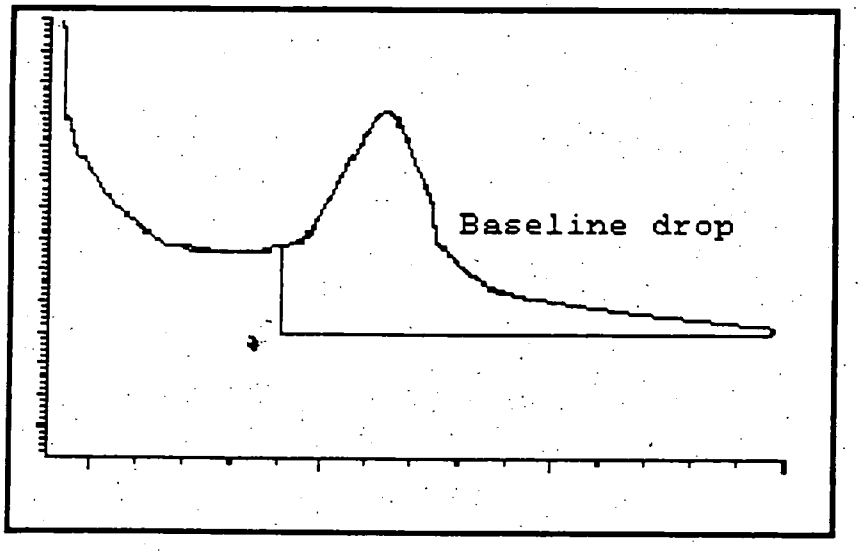


Allowable Integration

Baseline Shift

Attachment 6

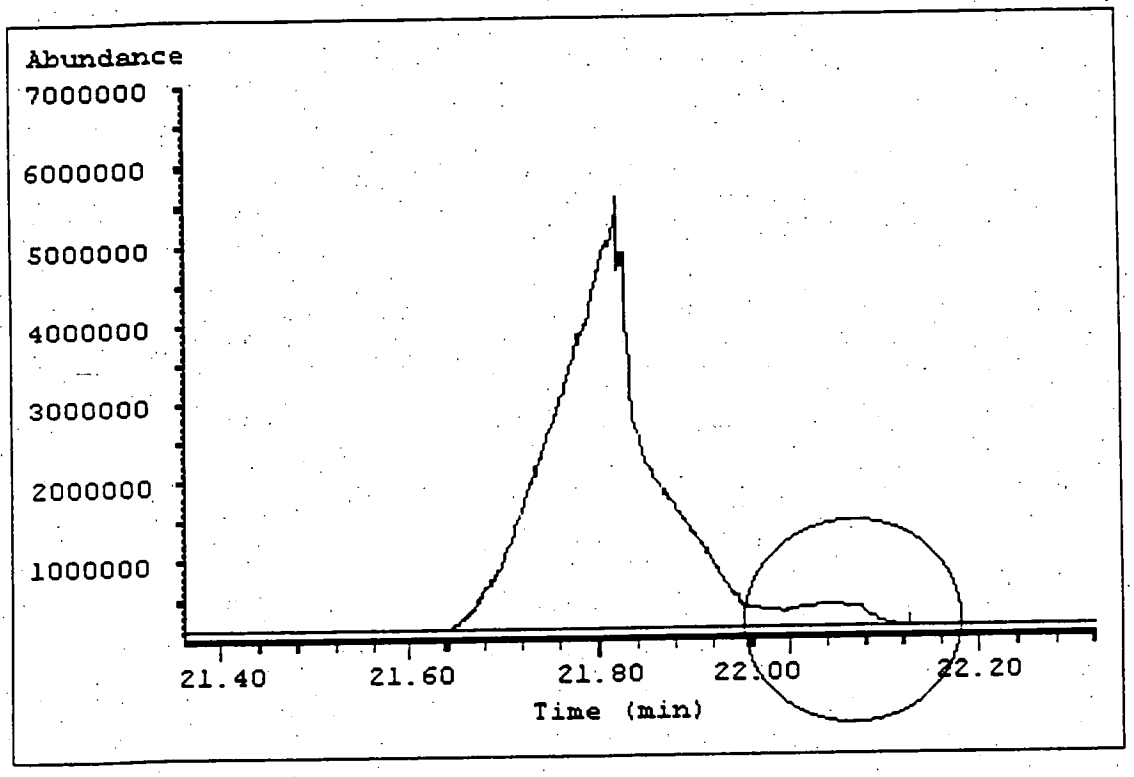




Allowable Integration

Skimming vs Baseline Drop

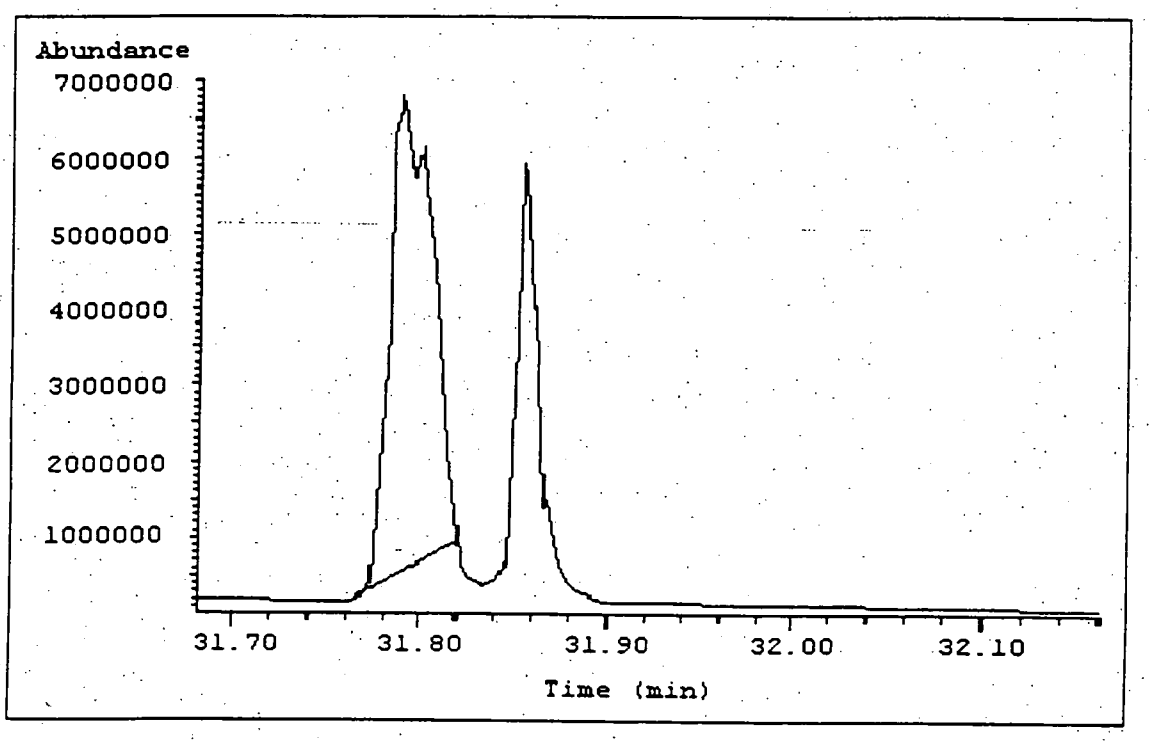
Attachment 7



Improper Integration

Adding Area by Including Other Peaks

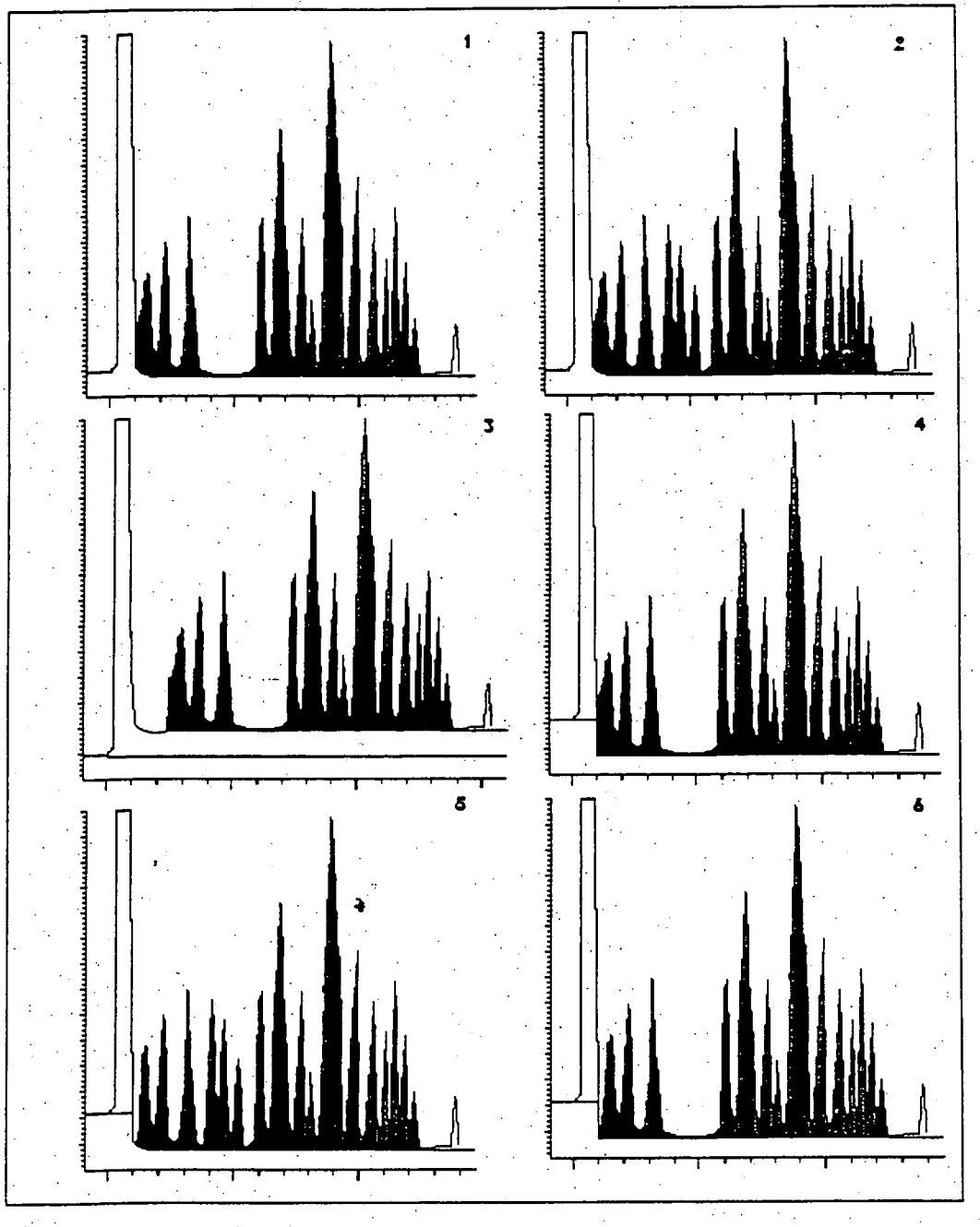
Attachment 8



Improper Integration

Baseline Moved To Decrease Peak Area

Attachment 9



Acceptable Methods of Integration
Grouped Peaks

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-2001

Title: **Waste Segregation and Disposal**

Revision history:

Number	Date
1	4/10/91
2	9/11/91
3	4/26/94
4	4/09/97
5	5/12/98

Written by: Harry Romberg Date: 6-2-98
Harry Romberg, Quality Assurance Officer

Approved by: Kathy Kreps Date: 6-2-98
Kathy Kreps, Laboratory Director

Controlled Document

No. 20 **Assigned to:** Tetra

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1. Introduction and Scope

1.1 Method Description

1.1.1 The purpose of this SOP is to describe the laboratory waste disposal scheme currently in place at Laucks. The primary waste streams described include solvents, PCB oil wastes, COD and TOC waste and soil samples. This SOP only covers handling of the waste from the point of collection.

1.1.2 This method is restricted to use by, or under the supervision of analysts experienced in the techniques described. As part of their training for analytical tasks which generate related wastes, each analyst must be trained to properly dispose of the waste or to the consolidate it at the appropriate collection point.

1.1.3 This SOP generally does not cover handling of the waste up to the point of disposal.

2. Equipment List

2.1 Equipment

2.1.1 The equipment necessary to properly dispose of laboratory wastes varies with the type of waste. In general, an appropriate container, packing material, and safety equipment (including clothing, eye wear, and respirators) is required.

3. Safety precautions

3.1 Safety Precautions

3.1.1 Solvent wastes may contain materials flammable at room temperature or lower. Caution should be taken to avoid flames and sparks when in the presence of or handling these wastes.

3.1.2 COD and TOC wastes may contain materials which will burn the skin, eyes, and/or mucous membranes if improperly handled. Precautions should be taken to avoid accidental contact.

3.1.3 All wastes may contain materials which can have both known and unknown long-term health effects. COD and TOC wastes, for instance, contain high levels of mercury salts. Direct contact should be avoided through the use of proper clothing and eye wear, even if no immediate danger is obvious. In the case of volatile solvents and other materials, handling should be done in a well-ventilated area and the exposure to vapors minimized. Where strong fumes are unavoidable, a carbon-filter or other respirator should be worn.

3.1.4 All people who handle waste products or the original reagents should be aware that the laboratory provides safety equipment and has a file containing Material Safety Data Sheets (MSDSs) on all laboratory chemicals in support of OSHA and other safety programs.

4. Operation procedures

4.1 Operations Appropriate to All Collection Areas

4.1.1 Land Disposal Restriction Forms (LDRs), manifests and other paperwork are not extensively discussed in this SOP because the disposal vendor deals with this aspect of the paperwork. It will only be necessary for the person who will be asked by the vendor to sign these forms (usually QA) to check that the information on the forms is accurate and to sign the form.

4.1.2 All waste requiring a Hazardous Waste disposal sticker and manifest will be marked with one of two EPA Hazardous Waste Site numbers. All waste transported from the 921 facility will be numbered WAD981762024 and all waste transported from the 940 facility will be numbered WAD027446608.

4.1.3 The Hazardous Waste Sticker must be labeled with the proper DOT shipping name, even though the disposal company will usually replace the label before shipping. The proper shipping names are listed below in the applicable sections of this SOP.

4.1.4 All collection drums **must** be marked with an appropriately filled out Hazardous Waste sticker (see Appendix A). It is only necessary for Laucks staff to fill in the date that collection was **started** and the contents of the drum in the appropriate space. Hazardous Waste cannot be accumulated for longer than 90 days before it must be disposed. Therefore, do **not** mark the date on the drum until collection is started so as to maximize the allowable time until disposal. This sticker will be replaced by the transporter when they arrive to transport the waste to an approved disposal facility. The replacement sticker will contain all of the information required for transport and disposal.

4.1.5 In addition, corrosive and flammable waste collection drums must have a sticker which indicates their corrosive or flammable nature (see Appendix B).

4.1.6 Once a material has been designated as waste and disposed into the designated drum, that drum must not be stored for longer than 90 days from the point that collection was **started**. This is rarely of concern at Laucks because transport is generally scheduled for most wastes within much less time than the required maximum storage time.

4.1.6.1 The one variation from the above rule is the TOC waste drum. This drum is not a satellite collection point but is actually the catch drum for the waste directly from the instrument. It will be disposed as soon as possible after it has reached capacity.

4.1.7 When collection drums are full or the 90-day limit is approaching, the Quality Assurance (QA) Department must be notified. The preferred lead-time for pickup is 10 working days so QA should actually be contacted 80 days after collection is

initiated. This department, at the time of this writing, is responsible for contacting the appropriate approved transporter and insuring proper disposal takes place.

4.1.8 All questions or concerns regarding hazardous waste operations should first be directed to QA who will determine the appropriate course of action.

4.2 Mixed Solvent Waste

4.2.1 This waste stream is primarily composed of methylene chloride with some acetone and hexane and potentially small quantities of other solvents or dissolved products. The collection point for all of this waste is in the 921 facility (Extractions) solvent locker.

4.2.2 Small, 5 gallon or less containers of other mixed solvent waste may be collected as satellite accumulation units in the inorganics or organics instrument preparation areas but these **must** be transported to the primary drums in Extractions when full. Satellite accumulation containers must be kept closed when not in use and must be marked with the words "Hazardous Waste" or with other words that identify the contents of the container. This will most conveniently be done by using a blank Hazardous Waste Sticker.

4.2.3 When new materials are collected in the primary drum, a Hazardous Waste sticker should be affixed with an initial collection date. The Hazardous Waste stickers should be marked with a DOT shipping name of "**Waste Flammable Liquids**".

4.2.4 Although methylene chloride is non-flammable, other components of these waste drums may be highly flammable. Thus, all of the waste solvent containers must be labeled as flammable.

4.2.5 At least 2 inches of headspace must be left between the top of the liquid and the top of the drum to allow for expansion.

4.2.6 When 3 or more full 55 gallon drums of this waste have been accumulated or 80 days have passed since the beginning of collection of the oldest accumulated drum, QA must be contacted to arrange for transport and disposal.

4.2.7 At the time of this writing, Laucks uses Laidlaw Environmental as the facility of choice for handling this waste stream, although this could be changed at the discretion of QA on either a one-time or ongoing basis.

4.3 Chemical Oxygen Demand (COD) Waste

4.3.1 The primary constituents of this waste are sulfuric acid, water, mercury, silver, and chromium (both tri- and hexavalent). The collection point for this waste is in the inorganics area where CODs are analyzed. These analyses are conducted in small pre-packaged tubes. The reacted tubes are not considered to be waste until they are poured out of the tubes into a collection container.

4.3.2 Collection containers must be labeled with a Hazardous Waste sticker as previously noted. The Hazardous Waste Sticker should be marked with a DOT shipping name of "**Waste Corrosive Liquids, Acidic, Inorganic**".

4.3.3 In addition to the hazardous waste sticker, these containers should be labeled as corrosive with the appropriate sticker as previously noted.

4.3.4 The waste not held for more than 90 days from initial collection (after pouring from the reaction tubes) until transportation for disposal. After 80 days have passed since the beginning of collection, QA must be contacted to arrange for transport and disposal within the allowable timeframe.

4.3.5 At least 2 inches of headspace must be left between the top of the liquid and the top of the drum to allow for expansion.

4.3.6 At the time of this writing, Laucks uses Laidlaw Environmental as the facility of choice for handling this waste stream. This vendor can be changed at the discretion of QA on either a one-time or ongoing basis.

4.4 Total Organic Carbon (TOC) Waste

4.4.1 The primary constituents of this waste are mercury, potassium persulfate, nitric acid, and water. This waste is collected directly from the instrument into a waste container beneath the instrument.

4.4.2 As this is a continuous process, Laucks does not begin the 90 day clock before disposal is required until this container is full. However, the container must be marked with a corrosive sticker. The Hazardous Waste sticker, in this case, must be dated as soon as the container is full and affixed at that time. The Hazardous Waste Sticker should be marked with a DOT shipping name of "**Waste Corrosive Liquids, Acidic, Inorganic**".

4.4.3 At least 2 inches of headspace must be left between the top of the liquid and the top of the container to allow for expansion.

4.4.4 As soon as the container is full, the QA department must be notified to arrange for disposal. This waste stream will generally not be held in storage for very long after collection.

4.4.5 At the time of this writing, Laucks uses Laidlaw Environmental as the vendor of choice for handling this waste stream. This vendor can be changed at the discretion of QA on either a one-time or ongoing basis.

4.5 Soil Sample Disposal

4.5.1 State law allows a laboratory to store samples and other materials indefinitely, until they are considered waste and disposed. After that time, from the date of first accumulation, a 90 day timeframe is allowed before disposal must occur. Thus, soils

should not be disposed of until enough have been accumulated to fill at least one 55 gal. drum.

4.5.2 Each drum used for soil waste disposal must be clearly marked with an identifying number which will be used to track which drum contained which samples. When samples are signed-out from their storage areas for disposal, the log sheet must be appropriate marked with the assigned drum number. This will enable the laboratory to track which samples were disposed in which drum.

4.5.2.1 The drums should be marked with a year, location from which they originate, and sequential number. Thus drums for which accumulation began in 1998 from the extractions laboratory would be marked 98-921-01. The -01 being a sequential number that would be incremented with each additional drum -02, -03, etc. throughout 1998. A drum from the main lab would be designated 98-940-01, etc.

4.5.2.2 When samples are transferred from the storage locations to the drums, the Secure Storage Custody Log must be marked to indicate into which drum they were disposed. This should include any bottle identifiers, if necessary to identify just what was disposed. Thus, it will be necessary for personnel disposing of samples to check the drums to make sure there is enough room for the designated samples. Soil samples will generally have their lids removed and disposed in the regular garbage. The jar and all will then be disposed in the waste drum. If the lids themselves contain client identifying marks or locations or have significant amounts of adhering material (oil, etc.) which cannot be readily dumped into the drum the lid will also be disposed into the waste drum.

4.5.2.3 When the drums are disposed, it will be necessary for the laboratory representative who signs the manifest to mark the drum identity on the manifest, although this only needs to be on the laboratory copy if the transporter does not want this information to appear on their copy of the record.

4.5.3 QA must be notified 80 days after accumulation has begun in order to arrange for disposal in a timely manner. If samples are not disposed until there is enough to fill a drum, this timeframe is not of major concern because there are always Hazardous Waste pickups scheduled within any 90 day time period.

4.5.4 The only stickers these drums must have is the Hazardous Waste sticker with the date accumulation was started clearly marked. The Hazardous Waste Sticker should be marked with a DOT shipping name of "**Waste Environmentally Hazardous Substances**".

4.5.5 At the time of this writing, Laucks uses Laidlaw Environmental as the vendor of choice for handling this waste stream, although this could be changed at the discretion of QA on either a one-time or ongoing basis. This vendor incinerates these soils prior

to landfilling which should dispose of any organic materials, including labels, oily material and other hazardous organic substances.

4.6 PCB Oil Waste Disposal

4.6.1 Laucks no longer analyzes many oil samples for PCBs. Thus, this is a very small and infrequent waste stream. However, discussion is presented here in order that there be some documented course of action when it is necessary to dispose of these materials.

4.6.2 All oil samples which are analyzed for PCBs or otherwise known to contain PCBs are treated as PCB oils. No effort is made to distinguish those that actually do contain PCBs.

4.6.3 These oils are accumulated in a 5 gal. drum located in the Extractions laboratory warehouse. This metal drum is stored inside of the lower half of a cut-off plastic 55 gal. drum which fulfills the federal requirements for secondary containment during storage.

4.6.4 When a full drum has been accumulated, Eastern Electric is contacted for pickup and disposal. A signed receipt must be obtained as proof of disposal. Eastern Electric sends a manifest in subsequent mail within 35 days of waste pick-up and must also send a certificate of disposal within 30 days after the actual disposal date.

4.6.5 No annual report to the Department of Ecology is required because the level of PCBs is considered so high as to fall outside of the state's responsibility to monitor. At such levels the federal government regulates the disposal under TSCA. For this reason, it also does not fall within the federal requirement for RCRA governed waste disposal within 90 days. Eastern Electric is responsible for filing appropriate reports. TSCA regulations require that manifests and certificates of disposal be kept on file for a minimum of 3 years.

5. Reports

5.1 Disposal Paperwork

5.1.1 Our current vendor produce all of the required paperwork and insure all of the appropriate container markings (stickers, etc.) are in place prior to shipment. Since Laucks' waste streams are consistent from time to time, our vendors already have the information required to properly fill out the paperwork and Hazardous Waste stickers.

5.1.1.1 The paperwork includes the manifests, land disposal restriction forms and other shipping paperwork. Thus the only requirements of the laboratory are to insure the paperwork is accurate and to sign the appropriate forms.

5.1.2 After the waste has been transported to the disposal or accumulation facility, a signed manifest is returned to the laboratory. This is kept with the permanent record.

5.1.3 All certificates of disposal later provided by the disposal vendor are also associated with any waste shipment and kept with the permanent record.

5.1.4 All records are retained for at least 5 years from the date of shipment of the waste.

5.2 Annual Reporting Requirements

5.2.1 The laboratory must file an annual report with the Washington Department of Ecology (WDOE) for legal and tax purposes. This report is due on March 1 each year. Reports are filed for both the 940 and the 921 facilities (both EPA ID numbers). All waste transported from the 921 facility will be numbered WAD981762024 and all waste transported from the 940 facility will be numbered WAD027446608.

5.2.1.1 The only exception to this reporting requirement is the reporting of the PCB waste oil which is a federally regulated waste and is thus not reported to the WDOE.

5.2.2 The format of this report is defined by WDOE in books provided to the laboratory several months in advance of the due date. Details of this report are not provided in this SOP.

5.2.3 In addition, as part of a WDOE program to reduce hazardous waste in general, Laucks files an annual pollution prevention plan update in September of each year. This report is more loosely defined and the only major requirement is that it be filed. Details of this report are not part of this SOP.

Appendix I

Hazardous Waste Sticker

See directions in this SOP for proper filling out of this sticker.

HAZARDOUS WASTE

FEDERAL LAW PROHIBITS IMPROPER DISPOSAL

IF FOUND, CONTACT THE NEAREST POLICE, OR
PUBLIC SAFETY AUTHORITY, OR THE
U.S. ENVIRONMENTAL PROTECTION AGENCY

PROPER D.O.T.
SHIPPING NAME_____ UN OR NA#_____

GENERATOR INFORMATION:

NAME_____

ADDRESS_____

CITY_____ STATE_____ ZIP_____

EPA
ID NO._____

EPA
WASTE NO._____

ACCUMULATION
START DATE_____

MANIFEST
DOCUMENT NO._____

HANDLE WITH CARE!

CONTAINS HAZARDOUS OR TOXIC WASTES

STYLE WM-6

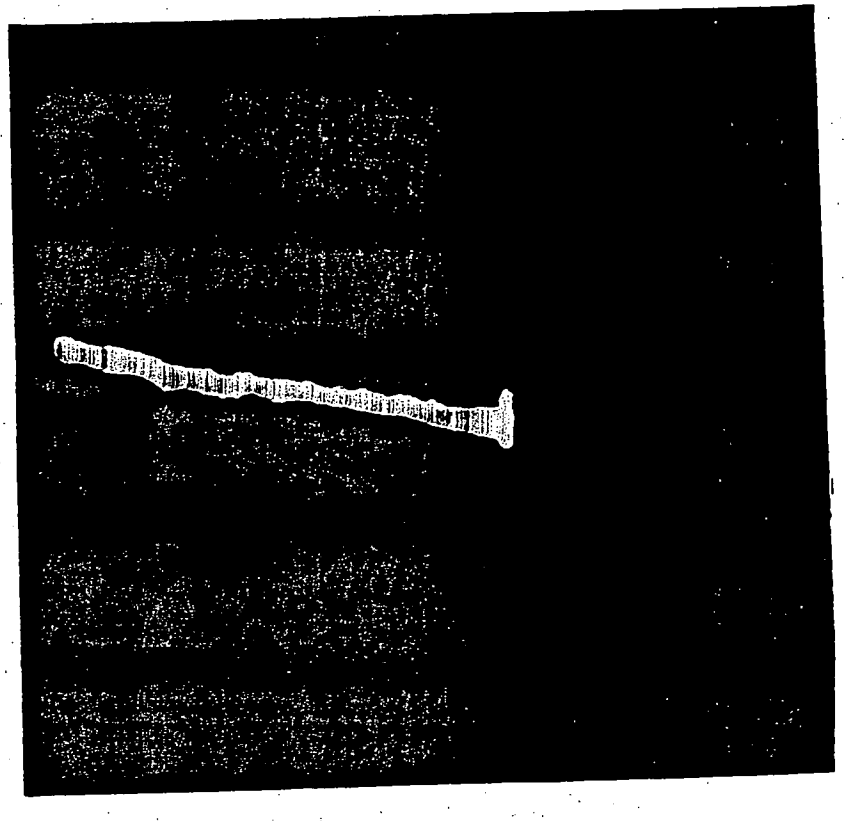
Printed by LABELMASTER, Div. of AMERICAN LABELMARK CO., INC., CHICAGO, IL 60646

Appendix II

Corrosive and Flammable Stickers

8-HML

Published by J. J. KELLER & ASSOCIATES, INC.
Neenah, WI 54956-0368 •(414)722-2848



Extraction Method for Base, Acid and Neutral Compounds in Water (8270C by 3520C)

Method # LTL-3000

May 27, 1998

UNCONTROLLED

Revision Number: #11

Written by: _____ Date: 5-27-98

Reviewed by: _____ Date: 5-27-98

Approved by: _____ Date: 5-28-98

1. **PURPOSE** - In this method, base, acid and neutral compounds are extracted at pH <2 and >11 with methylene chloride using a continuous liquid-liquid extractor. Extracts are dehydrated and concentrated in a Kuderna-Danish (K-D) apparatus for analysis by GC/MS.

2. **SAFETY** - During the conduct of this method, the extractionist will be exposed to a variety of reagent chemicals and solvents. The health effects of these various chemicals may be ascertained by reading the material safety data sheets (MSDS) available in the general files. Additionally, the samples by their very nature, may contain significant levels of hazardous materials. It is incumbent on each extractionist to exercise due care and caution while executing this method. The company will provide any protective equipment or clothing to assure employee safety.

3. **REAGENTS**

3.1. All reagents shall be of AR grade or better.

3.2. All solvents shall be distilled in glass unless otherwise indicated.

3.3. The following special reagents shall be prepared:

3.3.1 1:1 Sulfuric Acid - measure equal volumes of concentrated sulfuric acid and DIW. Note: Observe proper acid preparation techniques.

3.3.2. 10 N Sodium Hydroxide - weigh 400 grams sodium hydroxide, dissolve and dilute to one liter with DIW.

3.3.3. Anhydrous Sodium Sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400°C.

3.3.4. Surrogate solution prepared in methanol:

Base/Neutrals	Nitrobenzene-d5	200 ug/ml
	p-Terphenyl-d14	200 ug/ml
	2- Fluorobiphenyl	200 ug/ml
	1,2-Dichlorobenzene-d4	200 ug/ml
Acids	Phenol-d6	300 ug/ml
	2,4,6-Tribromophenol	300 ug/ml
	2-Fluorophenol	300 ug/ml
	2-Chlorophenol-d4	300 ug/ml

3.3.5. Matrix spiking solution prepared in methanol:

Base/Neutrals	1,2,4-Trichlorobenzene	100 ug/ml
	Acenaphthene	100 ug/ml
	2,4-Dinitrotoluene	100 ug/ml

	Pyrene	100 ug/ml
	n-Nitroso-di-n-propylamine	100 ug/ml
	1,4-Dichlorobenzene	100 ug/ml
Acids	Pentachlorophenol	150 ug/ml
	Phenol	150 ug/ml
	2-Chlorophenol	150 ug/ml
	4-Chloro-3-methylphenol	150 ug/ml
	4-Nitrophenol	150 ug/ml

4. EQUIPMENT

4.1. Continuous liquid-liquid extractor with 500 ml round, flat-bottom boiling flask

4.2. Organomations Assoc., Inc. - N-EVAP, (nitrogen evaporator), Model 112

4.3. Standard laboratory glassware to include:

4.3.1. K-D apparatus: 500 ml. K-D flask, 10 ml or 25 ml ampule and three-ball snyder column.

4.4. All glassware to be rinsed as follows, prior to use:

4.4.1. Technical grade acetone (if the glassware is wet).

4.4.2. Triple rinsed with methylene chloride.

4.5. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

5. QUALITY CONTROL

QUALITY CONTROL - The normal level of quality control will consist of blanks, blank spikes, matrix spikes and matrix spike duplicates (MS and MSD). This is performed on a per batch basis to include no more than 20 samples. The level of quality control will be indicated to the extractionist at the time the job is assigned. These samples serve to provide a measure of the recovery efficiency for the analyte and to provide data for statistical evaluation of the sample. In those instances that a client requires additional or different quality control measures, the extractionist will be directed accordingly in writing.

6. METHODOLOGY

6.1. Sample Extraction:

6.1.1. Mix sample thoroughly in its original container.

6.1.2. Measure 1000 ml sample into a graduated cylinder.

6.1.3. Quantitatively transfer the sample into a liquid-liquid extractor.

6.1.4. Prepare a blank and a blank spike with 1000 ml DIW.

6.1.5. Prepare two additional aliquots of one sample if Quality Control is required.

6.1.6. Pipet 250 ul surrogate solution into each extractor.

6.1.7. Pipet 250 ul matrix spiking solution into each QC extractor.

NOTE: If the possibility exists that the extract will require GPC cleanup (Method 3640, LTL-3692), add twice the amount of surrogate and spike.

6.1.8. Adjust the sample to pH <2 with 1:1 sulfuric acid.

6.1.9. Add 300 ml methylene chloride and boiling chips to a round, flat-bottom boiling flask.

6.1.10. Turn on the water recirculator and extract samples for 18 hours.

6.1.11. Allow the assembly to cool.

6.1.12 Remove boiling flask.

6.1.13. Adjust the sample to pH >11 with 10 N sodium hydroxide.

6.1.14. Turn on the water recirculator and extract samples for 18 hours

6.1.15. Allow the assembly to cool and collect all solvent in the boiling flask.

6.2. Solvent Dehydration

6.2.1. Prepare a glass funnel by plugging with glass wool, and filling 1/2-2/3 full with sodium sulfate.

6.2.2. Pre-rinse the sodium sulfate by passing 40 ml methylene chloride through the prepared funnel.

6.2.3. Pass the extract from step 6.1.15. through the funnel and collect in an assembled K-D apparatus.

6.2.4. Rinse the collection vessel with several 10 ml methylene chloride rinses.

6.2.5. Rinse the sodium sulfate with 40 ml of methylene chloride.

6.3. Solvent Evaporation

6.3.1. Assemble the full K-D apparatus with a snyder column prewet with 2-3 ml of methylene chloride.

6.3.2. Immerse K-D apparatus into a hot water bath, using a bath temperature of 90° C, with a long ampule immersed to a depth of 8 ml. Regulate the evaporation time to take one to one and a half hours.

6.3.3. Reduce the volume to 4-5 ml, remove the apparatus from the water bath and cool to room temperature.

6.3.4. Rinse joint and remove the snyder column. Allow rinse solvent to drain into ampule.

6.3.5. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of methylene chloride.

6.3.6. Reduce the extract volume to 1.0 ml in a warm water bath with nitrogen. Rinse internal walls of ampule several times during blowdown.

6.3.7. Transfer extract to a 1.8 ml vial. The final volume is then adjusted to 1.0 ml (as compared to a measured volume).

6.3.8. Label the extract and deliver to 940.

6.3.9. Complete all paperwork and bench sheet. Bench sheet to include time and date of start and finish of the extraction, extract location, as well as time and date of transfer to 940. Clip T-card on the folder and place in GC/MS room extraction folder box. File folder color is dark blue and blank name ____MSVWL_.

7. **ANALYSIS TIME** - Based on experience in the laboratory, it is anticipated that a single sample may be completed in approximately twenty four hours. If it is possible to batch similar samples, it is expected that about ten samples could be completed in approximately thirty hours. About two hours of actual hands on time will be expended by the extractionist if the clean ups are not necessary. These approximate times are based on the assumption that the samples are "average", and will not require significant additional time beyond normal operations. Additional time must be allocated for samples which are very dirty or are extraordinary.

8. **REFERENCES** - The following USEPA methods are the official methods on which this Laucks Testing Laboratory method is based. The primary methods are those which most closely parallel the Laucks procedure and are referenced by their USEPA series and number. In those instances for which there are no official EPA methods, the most suitable reference is given under the miscellaneous references section. The additional reference section cites those methods which contain additional information. These methods will frequently be official methods, which apply in part to, or support the Laucks method.

PRIMARY REFERENCES:

Test Methods for Evaluating Solid Waste, USEPA, SW-846.
3520C (1996), 8270C (1996)

Extraction Method for Polynuclear Aromatics in Water
(8270C by 3520C)

Method # LTL-3001

January 24, 2000

Revision Number: #3

Written by: _____ Date: 1-24-00

Reviewed by: _____ Date: 3-2-2000

Approved by: _____ Date: 3-3-2000

1. **PURPOSE** - In this method, polynuclear aromatics are extracted at pH <2 with methylene chloride using a continuous liquid-liquid extractor. Extracts are dehydrated and concentrated in a Kuderna-Danish (K-D) apparatus for analysis by GC/MS. This method also includes low concentration (SIM).

2. **SAFETY** - During the conduct of this method, the extractionist will be exposed to a variety of reagent chemicals and solvents. The health effects of these various chemicals may be ascertained by reading the material safety data sheets (MSDS) available in the general files. Additionally, the samples by their very nature, may contain significant levels of hazardous materials. It is incumbent on each extractionist to exercise due care and caution while executing this method. The company will provide any protective equipment or clothing to assure employee safety.

3. **REAGENTS**

3.1. All reagents shall be of AR grade or better.

3.2. All solvents shall be distilled in glass unless otherwise indicated.

3.3. The following special reagents shall be prepared:

3.3.1 1:1 Sulfuric Acid - measure equal volumes of concentrated sulfuric acid and DIW. Note: Observe proper acid preparation techniques.

3.3.2. Anhydrous Sodium Sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400° C.

3.3.3. Alumina, Neutral, Brockman Activity I - activate 60-325 mesh alumina by heating for 16 hours at 130° C.

3.3.4. Surrogate solution prepared in methanol:

1-Fluoronaphthalene	250 ug/ml
Fluorene-d10	250 ug/ml
Pyrene-d10	250 ug/ml

Low Concentration (SIM) surrogate solution prepared in methanol:

1-Fluoronaphthalene	5.0 ug/ml
Fluorene-d10	5.0 ug/ml
Pyrene-d10	5.0 ug/ml

3.3.5. Matrix spiking solution and Low Concentration (SIM) matrix spiking solution prepared in methanol:

Acenaphthene	50 ug/ml
Acenaphthylene	50 ug/ml
Anthracene	50 ug/ml

Benzo(a)anthracene	50 ug/ml
Benzo(a)pyrene	50 ug/ml
Benzo(b)fluoranthene	50 ug/ml
Benzo(ghi)perylene	50 ug/ml
Benzo(k)fluoranthene	50 ug/ml
Chrysene	50 ug/ml
Dibenzo(a,h)anthracene	50 ug/ml
Fluoranthene	50 ug/ml
Fluorene	50 ug/ml
Indeno(1,2,3-cd)pyrene	50 ug/ml
Naphthalene	50 ug/ml
Phenanthrene	50 ug/ml
Pyrene	50 ug/ml
2-Methylnaphthalene	50 ug/ml

4. EQUIPMENT

4.1. Continuous liquid-liquid extractor with 500 ml round, flat-bottom boiling flask

4.2. Organomations Assoc., Inc. - N-EVAP, (nitrogen evaporator), Model 112

4.3. Teflon thistle tube

4.4. Standard laboratory glassware to include:

4.4.1. K-D apparatus: 500 ml. K-D flask, 10 ml or 25 ml ampule and three-ball snyder column.

4.4.2. Monstr-pette disposable pipettes.

4.5. All glassware to be rinsed as follows, prior to use:

4.5.1. Technical grade acetone (if the glassware is wet).

4.5.2. Triple rinsed with methylene chloride.

4.6. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

5. **QUALITY CONTROL** - The normal level of quality control will consist of blanks, blank spikes, matrix spikes and matrix spike duplicates (MS and MSD). This is performed on a per batch basis to include no more than 20 samples. The level of quality control will be indicated to the extractionist at the time the job is assigned. These samples serve to provide a measure of the recovery efficiency for the analyte and to provide data for statistical evaluation of the sample. In those instances that a client requires additional or different quality control measures, the extractionist will be directed accordingly in writing.

6. METHODOLOGY

6.1. Sample Extraction:

6.1.1. Mix sample thoroughly in its original container.

6.1.2. Measure 1000 ml sample into a graduated cylinder.

6.1.3. Quantitatively transfer the sample into a liquid-liquid extractor.

6.1.4. Prepare a blank and a blank spike with 1000 ml DIW.

6.1.5. Prepare two additional aliquots of one sample if Quality Control is required.

6.1.6. Pipet 200 ul surrogate solution into each extractor.
(Low Conc: 250 ul of low conc. surrogate solution.)

6.1.7. Pipet 500 ul matrix spiking solution into each QC extractor.
(Low Conc: 25 ul of matrix spiking solution.)

6.1.8. Adjust the sample to pH <2 with 1:1 sulfuric acid.

6.1.9. Add 300 ml methylene chloride and boiling chips to a round, flat-bottom boiling flask.

6.1.10. Turn on the water recirculator and extract samples for 18 hours.

6.1.11. Allow the assembly to cool and collect all solvent in the boiling flask.

6.2. Solvent Dehydration

6.2.1. Prepare a glass funnel by plugging with glass wool, and filling 1/2-2/3 full with sodium sulfate.

6.2.2. Pre-rinse the sodium sulfate by passing 40 ml methylene chloride through the prepared funnel.

6.2.3. Pass the extract from step 6.1.11. through the funnel and collect in an assembled K-D apparatus.

6.2.4. Rinse the collection vessel with several 10 ml methylene chloride rinses.

6.2.5. Rinse the sodium sulfate with 40 ml of methylene chloride.

6.3. Solvent Evaporation

6.3.1. Assemble the full K-D apparatus with a snyder column prewet with 2-3 ml of methylene chloride.

6.3.2. Immerse K-D apparatus into a hot water bath, using a bath temperature of 90° C, with a long ampule immersed to a depth of 8 ml. Regulate the evaporation time to take one to one and a half hours.

6.3.3. Reduce the volume to 4-5 ml, remove the apparatus from the water bath and cool to room temperature.

6.3.4. Rinse joint and remove the snyder column. Allow rinse solvent to drain into ampule.

6.3.5. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of methylene chloride.

6.3.6. Reduce the extract volume to 1.0 ml in a warm water bath with nitrogen. Rinse internal walls of ampule several times during blowdown.

6.3.7. Transfer extract to a 1.8 ml vial. The final volume is then adjusted to 1.0 ml (as compared to a measured volume) in methylene chloride. Low Conc: Final volume adjusted to 0.5 ml. in methylene chloride.

NOTE: If there is significant color in the extract, an alumina cleanup (Method 3611B) is indicated.

6.4. Alumina Cleanup

6.4.1. Prepare a Monstr-pette column by plugging with a small amount of glass wool.

6.4.2. Pack column with a minimum of 3 gm. of activated alumina. Top with 1/2 cm of sodium sulfate.

6.4.3. Pre-elute column with 10 ml methylene chloride.

6.4.4. Add extract directly to top of the sodium sulfate and allow to elute onto the column.

6.4.5. Rinse the ampule twice with a small amount of methylene chloride and add to top of column.

6.4.6. Attach a Teflon thistle tube to the column and add a minimum of 10 ml methylene chloride.

6.4.7. Elute into a 16 x 125 mm culture tube.

6.4.8. Reduce the extract volume to 1.0 ml in a warm water bath with nitrogen. Rinse internal walls of the culture tube several times during blowdown.

6.4.9. Transfer extract to a 1.8 ml vial. The final volume is then adjusted to 1.0 ml (as compared to a measured volume) in methylene chloride. Low Conc: Final volume adjusted to 0.5 ml. in methylene chloride.

6.4.10. Label the extract and deliver to 940.

6.4.11. Complete all paperwork and bench sheet. Bench sheet to include extract location, as well as time and date of transfer to 940. Clip T-card on the folder and place in GC/MS room extraction folder box. File folder color is dark blue and blank name ____MPNWL_.

7. **REFERENCES** - The following USEPA methods are the official methods on which this Laucks Testing Laboratory method is based. The primary methods are those which most closely parallel the Laucks procedure and are referenced by their USEPA series and number. In those instances for which there are no official EPA methods, the most suitable reference is given under the miscellaneous references section. The additional reference section cites those methods which contain additional information. These methods will frequently be official methods, which apply in part to, or support the Laucks method.

PRIMARY REFERENCES:

Test Methods for Evaluating Solid Waste, USEPA, SW-846.

3520C (1996), 8270C (1996), 3611B (1996)

Extraction Method for Chlorinated Herbicide in Soil
(8151A by 3550B)

Method # LTL-3011

December 22, 1999

Revision Number: #1

Written by: _____ Date: 12-22-99

Reviewed by: _____ Date: 12-22-99

Approved by: _____ Date: 12-22-99

Controlled Document

No. 20 Assigned to: Tetra

1. **PURPOSE** - In this method, herbicides are extracted and esterified with diazomethane for analysis by GC/ECD.

2. **SAFETY** - During the conduct of this method, the extractionist will be exposed to a variety of reagent chemicals and solvents. The health effects of these various chemicals may be ascertained by reading the material safety data sheets (MSDS) available in the general files. Additionally, the samples, by their very nature, may contain significant levels of hazardous materials. It is incumbent on each extractionist to exercise due care and caution executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **MATERIALS**

3.1. All reagents are to be AR grade or better.

3.2. All solvents are to be distilled in glass unless otherwise noted.

3.3. The following special reagents should be prepared:

3.3.1. 1:1 methylene chloride/acetone (v/v)- prepared by mixing equal volumes of the solvents.

3.3.3. 12 N Sulfuric Acid - measure 334 mls of concentrated sulfuric acid and dilute to one liter with DIW. Note: Observe proper acid preparation techniques.

3.3.4. 10% Hydrochloric Acid - measure 100 ml concentrated hydrochloric acid and dilute to one liter with DIW. Note: Observe proper acid preparation techniques.

3.3.5. 37% Potassium Hydroxide - prepared by dissolving 376 grams potassium hydroxide pellets and diluting to one liter with DIW.

3.3.6. Anhydrous Sodium Sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400°C.

3.3.7. Acidified Sodium Sulfate - Weigh the anhydrous sodium sulfate (see 2.3.2.) in 100 gram increments into a suction flask. Cover the sodium sulfate with ethyl ether containing 0.1 ml concentrated sulfuric acid for each 100 g increment. Swirl the slurry for about two minutes then stopper the flask and apply an aspirator vacuum until the ether is removed . Place on a steam bath in a hood to assure that all ether is removed. Store in a closed bottle.

3.3.8. 10 M Potassium Hydroxide - prepared by dissolving 56.1 grams potassium hydroxide pellets and diluting to 100 ml with DIW.

3.3.9. Diazald® (Aldrich Chemical Co., Milwaukee, WI - catalog no. D2,800-0).

3.3.10. Silicic Acid - Activate and store at 130° C.

3.3.11. Surrogate solution prepared in methanol:

2,6-Dichlorobenzoic Acid	4.0 ug/ml
2,4-Dichlorophenyl Acetic Acid	8.0 ug/ml

3.3.12. Matrix Spiking solution prepared in methanol:

Pentachlorophenol	0.4 ug/ml
Picloram	2.0 ug/ml
2,4,5-TP	2.0 ug/ml
2,4,5-T	2.0 ug/ml
Dicamba	2.0 ug/ml
Dinoseb	4.0 ug/ml
2,4-DB	4.0 ug/ml
2,4-D	4.0 ug/ml
Dalapon	4.0 ug/ml
Dichloroprop	4.0 ug/ml
4-Nitrophenol	4.0 ug/ml
MCPP	200.0 ug/ml
MCPA	200.0 ug/ml

4. EQUIPMENT

4.1. Heat Systems Ultrasonic Processor - Model XL2020, 550 watts - Maintain per manufacturer's instructions.

4.1.1. 3/4 inch titanium horn (#208)

4.2. Glas-Col mechanical separatory funnel shaker

4.3. Organomations Assoc., Inc. - N-EVAP, (nitrogen evaporator), Model 112

4.4. Standard laboratory glassware to include:

4.4.1. 8 ounce extraction bottles

4.4.2. 300 ml Fleakers

4.4.1. 1000 ml Teflon separatory funnels

4.3.3. 500 ml Erlenmeyer flask

4.3.4. K-D apparatus: 250 and 500 ml. K-D flask, 10 ml or 25 ml ampule and three-ball snyder column

4.4. All glassware to be used shall be rinsed in the following manner:

4.4.1. 10% hydrochloric acid

4.4.2. Technical grade acetone

4.4.3. Triple rinsed with methylene chloride

4.5. Acid washed glass wool

4.6. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

5. **QUALITY CONTROL** - The normal level of quality control will consist of blank, blank spike, matrix spike and matrix spike duplicate (MS and MSD). This is performed on a per batch basis to include no more than 20 samples. The level of quality control will be indicated to the extractionist at the time the job is assigned. These samples serve to provide a measure of the recovery efficiency for the analyte and to provide data for statistical evaluation of the sample. In those instances that a client requires additional or different quality control measures, the extractionist will be directed accordingly in writing.

6. **METHODOLOGY**

6.1. Sample Extraction:

6.1.1. Mix the sample thoroughly in its original container if there is space available (otherwise mix in solvent rinsed aluminum tray).

6.1.2. Weigh 30.0 grams of soil (wet weight) into an extraction bottle.

6.1.3. Prepare two additional aliquots of a sample if Quality Control is required.

6.1.4. Prepare a blank and a blank spike with 60 grams acidified sodium sulfate.

6.1.5. Adjust the sample to pH < 2 with 1 ml concentrated hydrochloric acid.

6.1.6. Pipet 250 ul surrogate solution into each bottle.

6.1.7. Pipet 250 ul matrix spiking solution into each of the QC bottle.

6.1.8. Add approx. 30 grams acidified sodium sulfate and mix well to give the soil a sandy texture. Add more if necessary.

6.1.9. Add 100 ml 1:1 methylene chloride/acetone to each bottle.

6.1.10. Sonicate the bottles for 3 minutes using the sonic horn, set at 50% duty cycle and full output (10).

6.1.11. Centrifuge the samples for 20 minutes at 2000 rpm if necessary to achieve a partition.

6.1.12. Decant off and collect the supernatant in Erlenmeyer flask containing 10 grams acidified sodium sulfate.

6.1.13. Repeat from step 6.1.9. two additional times using 100 ml methylene chloride, combining all of the extracts.

6.1.14. Allow extract to remain in contact with the acidified sodium sulfate for a minimum of 2 hours, periodically swirling the extract and sodium sulfate. If sodium sulfate is not free flowing, add a few additional grams. Extract may be stored overnight.

6.2. Solvent dehydration

6.2.1. Prepare a glass funnel by plugging with acid washed glass wool and 10 grams acidified sodium sulfate.

6.2.2. Pre-rinse the sodium sulfate by passing 40 ml methylene chloride through the prepared funnel.

6.2.3. Pass the extract from step 6.1.14. through the funnel and collect in an assembled K-D apparatus.

6.2.4. Rinse the collection vessel with several 10 ml methylene chloride rinses.

6.2.5. Rinse the sodium sulfate with 40 ml of methylene chloride.

6.3. Solvent Evaporation

6.3.1. Assemble the full K-D apparatus with a Snyder column prewet with 2-3 ml of methylene chloride.

6.3.2. Immerse K-D apparatus into a hot water bath, using a bath temperature of 90° C, with a long ampule immersed to a depth of 12 ml. Regulate the evaporation time to take one to one and a half hours.

6.3.3. Reduce the volume to 4-5 ml and remove the apparatus from the water bath. Cool to room temperature.

6.3.4. Remove Snyder column and add additional boiling chips to flask.

6.4. Hydrolysis

6.4.1. Add 5 ml of 37% potassium hydroxide and 30 ml DIW to each K-D flask.

6.4.2. Add Snyder column and return to water bath for 90 minutes at 60 - 65°C.

6.4.3. Remove the apparatus from the water bath, and cool to room temperature.

6.4.4. Rinse joint with DIW and remove the snyder column. Allow rinse to drain into flask.

6.4.5. Transfer the hydrolyzed aqueous solution to a labeled 1000 ml separatory funnel.

6.4.6. Add 100 ml methylene chloride to each funnel.

6.4.7. Shake the samples hard for three minutes on the mechanical shaker, with the stopcocks closed.

6.4.8. Replace the funnels in rack and allow to stand for 10 minutes.

6.4.9. Drain and discard methylene chloride.

6.4.10. Repeat from step 6.4.6. for a total of three extractions.

6.4.11. Adjust pH to <2 with 5 ml cold (4° C) 12 N sulfuric acid.

6.4.12. Add 40 ml ethyl ether to each funnel.

6.4.13. Shake the samples for three minutes on the mechanical shaker, with the stopcocks open.

6.4.14. With stopcock closed, replace the funnels in rack and allow to stand for 10 minutes.

6.4.15. Drain the aqueous layer into a Fleaker and collect the ether layer into a separate labeled Fleaker containing 10 grams acidified sodium sulfate. Return the aqueous layer to the separatory funnel.

6.4.16. Repeat from step 6.4.12. two additional times with 20 ml ethyl ether, until a total of three extractions have been performed.

6.4.17. Allow extract to remain in contact with the acidified sodium sulfate for a minimum of 2 hours, periodically swirling the extract and sodium sulfate. If sodium sulfate is not free flowing, add a few additional grams. Extract may be stored overnight.

6.5. Extract Concentration

6.5.1. Transfer extract from step 6.4.17. to a K-D apparatus.

6.5.2. Return to water bath and K-D for 10 - 20 minutes at 60 - 65°C.

6.5.3. Reduce the volume to 3-4 ml and remove the apparatus from the water bath. Cool to room temperature.

6.5.4. Rinse joint with ethyl ether and remove the snyder column. Allow rinse to drain into flask.

6.5.5. Transfer the extract to a 16 x 100 mm culture tube.

6.5.6. Gently reduce volume to approx. 1 ml in nitrogen blowdown.

6.5.7. Add 1 ml iso-octane and bring to 4.0 ml with ethyl ether.

6.6. Derivatization:

6.6.1. Prepare a derivatization standard by adding 250 ul surrogate solution and 250 ul matrix spiking solution to 4.0 ml ethyl ether/iso-octane (see step 6.5.7.) in a 16 x 100 culture tube.

6.6.2. To tube A (the first tube in the train), add 1 ml methanol and approx. 8.0 ml with ethyl ether.

6.6.3. To tube B add:

6.6.3.1. 2.0 ml 10 M potassium hydroxide

6.6.3.2. 1.4 ml Carbitol (diethylene glycol monoethyl ether)

6.6.4. Place 10 ul micro-pipet in each sample tube from step 6.5.7.

6.6.5. Connect nitrogen line to the apparatus and regulate so that tube A bubbles actively but not violently.

6.6.6. Add 2 scoops (approximately 0.1-0.2 grams) of Diazald and 1.4 ml ethyl ether to tube B. Stopper.

6.6.7. Bubble the generated diazomethane into the tube for 90 seconds. (Extract will turn bright yellow.)

6.6.8. Let extract stand for 20 minutes.

6.6.9. Add 0.1 - 0.2 gm. activated silicic acid to each culture tube. Allow to stand until evolution of nitrogen gas has stopped. This may take several hours and may be stored overnight.

6.6.10. Adjust the final volume to 10.0 ml (as compared to a measured volume) with hexane.

6.6.11. Label the extract and deliver to 940.

6.6.12. Complete all the necessary paperwork and bench sheet. Bench sheet to include time and date of transfer to 940 and extract location. Clip the T-card on the folder and place in the GC room extraction folder box. The file folder color will be yellow, and the blank name will be ____GHB.SL_.

7. **ANALYSIS TIME** - Based on experience in the laboratory, it is anticipated that a single sample may be completed in about 24-26 hours. If it is possible to batch similar samples it is expected that about five samples could be completed in approximately 26-28 hours. About 90% of hands on time will be required of the extractionist. These approximations are based the assumption that the samples are "average", and will not require additional time beyond normal operations. Additional time must be allocated for samples which are very dirty or are extraordinary.

8. **REFERENCES** - The following USEPA methods are the official methods on which this Laucks Testing Laboratory method is based. The primary methods are those which most closely parallel the Laucks procedure and are referenced by their USEPA series and number. In those instances for which there are no official EPA methods, the most suitable reference is given under the miscellaneous references section. The additional reference section cites those methods which contain additional information. These methods will frequently be official methods, which apply in part to, or support the Laucks method.

PRIMARY REFERENCES:

Test Methods for Evaluating Solid Waste, USEPA, SW-846.

3550B (1996), 8151A (1996)

Extraction Method for Ordnance Compounds in Water (8330)

Method # LTL-3077

November 15, 1999

Revision Number: #4

Written by: B. O Gill Date: 11-15-99

Reviewed by: Harry Romberg Date: 11-16-99

Approved by: Kathy Steps Date: 11-23-99

Controlled Document

No. 20 Assigned to: Tetra

1. **PURPOSE** - In this method the ordnance compounds are extracted from neutral water with acetonitrile. The extract is salted-out and analyzed by HPLC.

2. **SAFETY** - During the conduct of this method, the extractionist will be exposed to a variety of reagent chemicals and solvents. The health effects of these various chemicals may be ascertained by reading the material safety data sheets (MSDS) available in the general files. Additionally, the samples by their very nature, may contain significant levels of hazardous materials. It is incumbent on each extractionist to exercise due care and caution while executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **REAGENTS**

3.1. All reagents shall be of AR grade or better.

3.2. All solvents shall be distilled in glass unless otherwise indicated.

3.3. The following special reagents shall be prepared:

3.3.1. Sodium Chloride - prepared by muffling AR grade sodium chloride for four hours at 400°C.

3.3.2. Salt Water - prepared by weighing 325 grams muffled sodium chloride, dissolving in DIW and bringing to 1000 ml.

3.3.3. Surrogate solution prepared in methanol:

1,2-Dinitrobenzene	400 ug/ml

3.3.4. Matrix spiking (MS) solution prepared in methanol:

1,3-Dinitrobenzene	40 ug/ml
2,4-Dinitrotoluene	40 ug/ml
2,6-Dinitrotoluene	40 ug/ml
HMX	40 ug/ml
RDX	40 ug/ml
Nitrobenzene	40 ug/ml
2-Nitrotoluene	40 ug/ml
3-Nitrotoluene	40 ug/ml
4-Nitrotoluene	40 ug/ml
Tetryl	40 ug/ml
TNT	40 ug/ml
1,3,5-Trinitrobenzene	40 ug/ml
2-amino-4,6-dinitrotoluene	40 ug/ml
4-amino-2,6-dinitrotoluene	40 ug/ml

3.3.5. Special Matrix spiking solution for PETN/NG in methanol:

PETN	25 ug/ml
Nitroglycerin	50 ug/ml

3.3.6. Special Matrix spiking solution for 6 additional compounds in methanol:

2,4-DA-6-NT	40 ug/ml
2,6-DA-4-NT	40 ug/ml
3,5-DNA	40 ug/ml
MNX	40 ug/ml
TNX	40 ug/ml
4,4'-TN-AZOXY	40 ug/ml

4. EQUIPMENT

4.1. Magnetic stirrer with stirring bar

4.2. Standard laboratory glassware to include:

4.2.1. 1000 ml volumetric flask and various sizes of graduated cylinders

4.3. All glassware to be rinsed as follows, prior to use:

4.3.1. Technical grade acetone (if the glassware is wet).

4.3.2. Triple rinsed with methylene chloride.

4.4. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

4.5. PTFE 0.45µm syringe filter.

5. QUALITY CONTROL

QUALITY CONTROL - The normal level of quality control will consist of blanks, blank spikes, matrix spikes and matrix spike duplicates (MS and MSD). This is performed on a per batch basis to include no more than 20 samples. The level of quality control will be indicated to the extractionist at the time the job is assigned. These samples serve to provide a measure of the recovery efficiency for the analyte and to provide data for statistical evaluation of the sample. In those instances that a client requires additional or different quality control measures, the extractionist will be directed accordingly in writing.

6. METHODOLOGY

6.1. Sample Extraction

6.1.1. Mix sample thoroughly in its original container.

6.1.2. Measure 770 mls sample into a 1000 ml volumetric flask placed on a magnetic stirrer.

6.1.3. Prepare two additional aliquots of one sample if Quality Control is required.

6.1.4. Prepare a blank and blank spike with DIW.

6.1.5. Pipet 50 ul surrogate solution to each flask.

6.1.6. Pipet 500 ul matrix spiking solution to each of the QC flasks. (When indicated, use 500 ul special matrix spiking solution.)

6.1.7. Add 251.3 gm sodium chloride to the flask with the stirring bar ~~at~~ maximum speed and stir until sodium chloride is completely dissolved.

6.1.8. Add 164 mls acetonitrile to each flask and stir for 15 minutes.

6.1.9. Turn off the stirrer and let set for 10 minutes.

6.1.10. Remove acetonitrile with a Pasteur pipet and transfer to a 100 ml flask.

6.1.11. Add 10 ml acetonitrile to the sample and stir for 15 minutes.

6.1.12. Turn off stirrer and let set for 10 minutes.

6.1.13. Transfer acetonitrile to flask with extract from step 6.1.10. Discard sample in 1000 ml flask.

6.1.14. Add 84 mls salt water to extract in flask.

6.1.15. Stir for 15 minutes and let stand for 10 minutes.

6.1.16. Transfer acetonitrile to a 10 ml graduated cylinder.

6.1.17. Add 1.0 ml acetonitrile to flask and repeat steps 6.1.15 and 6.1.16.

6.1.18. Record total final volume to 0.1 ml.

6.1.19. Transfer final extract to a 4.0 ml **amber** vial. Any remaining extract may be discarded. If extract is cloudy or turbid, filter through a PTFE 0.45µm syringe filter into amber vial.

6.1.20. Label the extract and deliver to 940.

6.1.21. Complete all paperwork and bench sheet. Bench sheet to include date and time of transfer to 940 and extract location. Clip the T-card on the folder and place in GC room extraction folder box. The file folder color will be red and the blank name will be ____HOR.WL_.

7. **ANALYSIS TIME** - Based on experience in the laboratory, it is anticipated that a single sample may be completed in approximately 3 hours. If it is possible to batch similar samples, it is expected that about ten samples could be completed in approximately 8 hours. About one hour of actual hands on time will be expended for a single sample by the extractionist. These approximate times are based on the assumption that the samples are "average", and will not require additional time beyond normal operations. Additional time must be allocated for samples which are very dirty or are extraordinary.

8. **REFERENCES** - The following USEPA methods are the official methods on which this Laucks Testing Laboratory method is based. The primary methods are those which most closely parallel the Laucks procedure and are referenced by their USEPA series and number. In those instances for which there are no official EPA methods, the most suitable reference is given under the miscellaneous references section. The additional reference section cites those methods which contain additional information. These methods will frequently be official methods, which apply in part to, or support the Laucks method.

PRIMARY REFERENCES:

Test Methods for Evaluating Solid Waste, USEPA, SW-846, Method 8330, (1994).

Extraction Method for Base, Acid and Neutral Compounds in Soil (8270C by 3550B)

Method # LTL-3100

April 28, 1998

UNCONTROLLED

Revision Number: #11

Written by: B. O. Gill Date: 4-28-98

Reviewed by: Harry Romberg Date: 4-28-98

Approved by: Kathy E Kreps Date: 5/1/98

1. **PURPOSE** - In this method base, acid and neutral compounds are extracted from neutral soils with a mixture of methylene chloride and acetone. The extract is dehydrated, concentrated in a Kuderna-Danish (K-D) apparatus and GPC cleaned prior to analysis by GC Mass Spectrometer. This method provides for soils of low and medium levels of contamination.

2. **SAFETY** - During the conduct of this method, the analyst will be exposed to a number of reagent chemicals and solvents. The health effects of these various chemicals may be ascertained by reading the material safety data sheets (MSDS) available in the general files. Additionally, the samples, by their very nature may contain significant levels of hazardous materials. It is incumbent on each analyst to exercise due care and caution executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **REAGENTS**

3.1. All reagents are to be AR grade or better.

3.2. All solvents are to be distilled in glass, unless otherwise noted.

3.3. The following special reagents should be prepared:

3.3.1. 1:1 methylene chloride/acetone (v/v)- prepared by mixing equal volumes of the solvents.

3.3.2. Anhydrous sodium sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400°C.

3.3.3. Surrogate solution prepared in methanol:

Base/Neutrals	Nitrobenzene-d5	200 ug/ml
	p-Terphenyl-d14	200 ug/ml
	2- Fluorobiphenyl	200 ug/ml
	1,2-Dichlorobenzene-d4	200 ug/ml
Acids	Phenol-d5	300 ug/ml
	2,4,6-Tribromophenol	300 ug/ml
	2-Fluorophenol	300 ug/ml
	2-Chlorophenol-d4	300 ug/ml

3.3.4. Matrix spiking solution prepared in methanol.

Base/Neutrals	1,2,4-Trichlorobenzene	100 ug/ml
	Acenaphthene	100 ug/ml
	2,4-Dinitrotoluene	100 ug/ml
	Pyrene	100 ug/ml
	n-Nitroso-di-n-propylamine	100 ug/ml
	1,4-Dichlorobenzene	100 ug/ml
Acids	Pentachlorophenol	150 ug/ml
	Phenol	150 ug/ml
	2-Chlorophenol	150 ug/ml
	4-Chloro-3-methyl phenol	150 ug/ml
	4-Nitrophenol	150 ug/ml

4. EQUIPMENT

4.1. Heat Systems Ultrasonic Processer - Model XL2020, 550 watts - Maintain per manufacturer's instructions.

4.1.1. 3/4 inch titanium horn (#208) for low concentrations

4.1.2. 1/8 inch tapered titanium microtip (#419) for medium concentrations

4.2. Analytical Biochemical Laboratories, Inc. (ABC) Model 1002B or Model 1000 Gel-Permeation Chromatography (GPC).

4.3. Organomations Assoc., Inc. - N-EVAP, (nitrogen evaporator), Model 112

4.4. Standard laboratory glassware to include:

4.4.1. 8 ounce extractions jars

4.4.2. 500 ml Fleakers

4.4.3. K-D apparatus: 500 ml. K-D flask, 10 ml or 25 ml ampule and three-ball snyder column.

4.5. All glassware to be rinsed as follows, prior to use:

4.5.1. Technical grade acetone (if the glassware is wet).

4.5.2. Triple rinsed with methylene chloride.

4.6. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

5. **QUALITY CONTROL** - The normal level of quality control will consist of blanks, blank spikes, matrix spikes and matrix spike duplicates (MS and MSD). This is performed on a per batch basis to include no more than 20 samples. The level of quality control will be indicated to the extractionist at the time the job is assigned. These samples serve to provide a measure of the recovery efficiency for the analyte and to provide data for statistical evaluation of the sample. In those instances that a client requires additional or different quality control measures, the extractionist will be directed accordingly in writing.

6. **METHODOLOGY**

NOTE: It is necessary to make an intuitive decision as to which level extraction procedure to follow. If the soil appears clean with little odor, do a low level extraction. If the soil has appreciable odor, is tar-like, partially miscible, or has an oily appearance, prep both a low and a medium level extraction. Totally miscible samples may only have a medium level extraction. Remember it is important that holding times be met. If you are in doubt, prep and store a medium level sample simultaneously.

6.1. Sample Extraction - Low Level Soils

6.1.1. Mix sample thoroughly in its original container if there is space available (otherwise mix in solvent rinsed aluminum tray).

6.1.2. Weigh 30.0 grams of soil (wet weight) into an extraction bottle.

6.1.3. Prepare two additional aliquots of a sample if Quality Control is required.

6.1.4. Add 30 to 60 grams sodium sulfate and mix well to give the soil a sandy texture.

6.1.5. Prepare a blank and a blank spike with 60 grams sodium sulfate.

6.1.6. Pipet 500 ul surrogate solution to each bottle.

6.1.7. Pipet 500 ul matrix spiking solution to each of the QC bottles.

6.1.8. Add 100 ml 1:1 methylene chloride/acetone to each bottle.

6.1.9. Sonicate the bottles for 3 minutes using the sonic horn, set at 50% duty cycle and full output (10).

6.1.10. Centrifuge the samples for 20 minutes at 2000 rpm if necessary to achieve a partition.

6.1.11. Decant off and collect the supernatant.

6.1.12. Repeat from step 6.1.8. two additional times, combining all of the extracts.

6.2. Solvent dehydration

6.2.1. Prepare a glass funnel by plugging with glass wool, and filling 1/2-2/3 full with sodium sulfate.

6.2.2. Pre-rinse the sodium sulfate by passing 40 ml methylene chloride through the prepared funnel.

6.2.3. Pass the extract from step 6.1.12. through the funnel and collect in an assembled K-D apparatus.

6.2.4. Rinse the collection vessel with several 10 ml methylene chloride rinses.

6.2.5. Rinse the sodium sulfate with 40 ml of methylene chloride.

6.3. Solvent Evaporation

6.3.1. Assemble the full K-D apparatus with a snyder column prewet with 2-3 ml of methylene chloride.

6.3.2. Immerse K-D apparatus into a hot water bath, using a bath temperature of 90° C, with a long ampule immersed to a depth of 12 ml. Regulate the evaporation time to take one to one and a half hours.

6.3.3. Reduce the volume to 4-5 ml and remove the apparatus from the water bath. Cool to room temperature.

6.3.4. Rinse joint and remove snyder column. Allow rinse solvent to drain into ampule.

6.3.5. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of solvent.

6.3.6. Reduce the extract volume to less than 8 ml on a nitrogen blowdown. Transfer extract to a 16 x 100 mm culture tube, and adjust to 10.0 ml intermediate volume (as compared to a measured volume) with methylene chloride.

6.3.7. At this point the extract will be GPC cleaned -- see Method # LTL-3692.

6.3.8. K-D the GPC cleaned extract. Reduce the extract to 1.0 ml in a warm water bath with nitrogen. Rinse internal walls of ampule several times during blowdown.

6.3.9. Transfer the extract to a 1.8 ml vial. The final volume is then adjusted to 1.0 ml (as compared to a measured volume) in methylene chloride.

6.3.10. Label the extract and deliver to 940.

6.3.11. Complete all paperwork and bench sheet. Bench sheet to include the date of GPC, date and time of transfer to 940 and extract location. Clip the T-Card on the folder and place in GC/MS room extraction folder box. The file folder color will be blue and the blank name will be ____MSV.SL_.

6.4. Sample Extraction - Medium Level Soils

6.4.1. Weigh 2.00 gram soil into a silanized scintillation vial.

6.4.2. Prepare two additional aliquots of a sample if Quality Control is required.

6.4.3. Add two grams sodium sulfate to all sample vials.

6.4.4. Prepare a blank and blank spike consisting of two grams of sodium sulfate.

6.4.5. Pipet 500 ul of the surrogate into each vial.

6.4.6. Pipet 500 ul matrix spiking solution into each of the QC vials.

6.4.7. Add 9.5 ml methylene chloride to each tube and 9.0 ml to each QC vial.

6.4.8. Sonicate the vials for 2 minutes using the sonic horn (microtip), set at 50% duty cycle and half output (5).

6.4.9. Loosely pack a Monstr-pipet column 1/3 full (approx. 3 cm) with solvent cleaned glass wool. Add approx. 1 cm sodium sulfate.

6.4.10. Place a 16 x 100 mm culture tube under the column.

6.4.11. Pass the extract through the column. Collect a minimum of 8.0 mls.

6.4.12. At this point the extract will be GPC cleaned -- see Method # LTL-3692.

6.4.13. K-D the GPC cleaned extract. Reduce the extract to 1.0 ml in a warm water bath with nitrogen. Rinse internal walls of ampule several times during blowdown.

6.4.14. Transfer the extract to a 1.8 ml vial. The final volume is then adjusted to 1.0 ml (as compared to a measured volume) in methylene chloride.

6.4.15. Label the extract and deliver to 940.

6.4.16. Complete all paperwork and bench sheet. Bench sheet to include the date of GPC, date and time of transfer to 940 and extract location. Clip the T-Card on the folder and place in GC/MS room extraction folder box. The file folder color blue and the blank name will be ____MSV.SM_.

7. **ANALYSIS TIME** - Based on extensive experience in the laboratory, it is anticipated that a single sample may be completed in about ten hours. If it is possible to batch similar samples, it is expected that about six samples could be completed in approximately 16 hours. About one and one half hours of hands on extractionist time will be required per sample. These approximations are based on the assumption that the samples are "average", and will not require additional time beyond normal operations.

8. **REFERENCES** - The following USEPA methods are the official methods on which this Laucks Testing Laboratory method is based. The primary methods are those which most closely parallel the Laucks procedure and are referenced by their USEPA series and number. In those instances for which there are no official EPA methods, the most suitable reference is given under the miscellaneous references section. The additional reference section cites those methods which contain additional information. These methods will frequently be official methods, which apply in part to, or support the Laucks method.

PRIMARY REFERENCES:

Test Methods for Evaluating Solid Waste, USEPA, SW-846 (1996)

8270C, 3550B

Extraction Method for Ordnance Compounds in Soils
(8330A)

Method # LTL-3161

February 17, 2000

Revision Number: #4

Written by: B. O Neal Date: 2-17-00

Reviewed by: Nancy Bradley Date: 2-17-2000

Approved by: Kathy Hayes Date: 02-17-2000

Controlled Document

No. 20 Assigned to: Tetra

1. **PURPOSE** - In this method the ordnance compounds are extracted from neutral soil with acetonitrile. The sample is air dried, sonicated, and extract salted-out and analyzed by HPLC.

2. **SAFETY** - During the conduct of this method, the extractionist will be exposed to a variety of reagent chemicals and solvents. The health effects of these various chemicals may be ascertained by reading the material safety data sheets (MSDS) available in the general files. Additionally, the samples by their very nature, may contain significant levels of hazardous materials. It is incumbent on each extractionist to exercise due care and caution while executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **REAGENTS**

3.1. All reagents shall be of AR grade or better.

3.2 . All solvents shall be distilled in glass unless otherwise indicated.

3.3. The following special reagents shall be prepared:

3.3.1. Ottawa Sand - prepared by soxhleting for 8 hours with methylene chloride and muffling for four hours at 400°C.

3.3.2. 0.045 M Calcium Chloride - prepared by dissolving 5.0 gm in 1000 ml of DIW.

3.3.3. Surrogate solution prepared in methanol:

1,2-Dinitrobenzene	400 ug/ml

3.3.4. Matrix spiking (MS) solution prepared in methanol:

1,3-Dinitrobenzene	40 ug/ml
2,4-Dinitrotoluene	40 ug/ml
2,6-Dinitrotoluene	40 ug/ml
HMX	40 ug/ml
RDX	40 ug/ml
Nitrobenzene	40 ug/ml
2-Nitrotoluene	40 ug/ml
3-Nitrotoluene	40 ug/ml
4-Nitrotoluene	40 ug/ml
Tetryl	40 ug/ml
TNT	40 ug/ml
1,3,5-Trinitrobenzene	40 ug/ml
2-amino-4,6-dinitrotoluene	40 ug/ml
4-amino-2,6-dinitrotoluene	40 ug/ml

4. EQUIPMENT

4.1. Ultrasonic bath

4.2. #30 mesh sieve

4.3. Disposable cartridge filters - 0.45 µm Teflon filter

4.4. Standard laboratory glassware to include:

4.4.1. 20 x 150 mm culture tubes

4.5. Volumetric measurements are to be made with graduated serological pipets or a calibrated fixed volume microdispenser and individually calibrated vials.

5. QUALITY CONTROL

- The normal level of quality control will consist of blanks, blank spikes, matrix spikes and matrix spike duplicates (MS and MSD). This is performed on a per batch basis to include no more than 20 samples. The level of quality control will be indicated to the extractionist at the time the job is assigned. These samples serve to provide a measure of the recovery efficiency for the analyte and to provide data for statistical evaluation of the sample. In those instances that a client requires additional or different quality control measures, the extractionist will be directed accordingly in writing.

6. METHODOLOGY

6.1. Sample Extraction

6.1.1. Mix sample thoroughly in its original container if there is space available (otherwise mix in solvent rinsed aluminum tray).

6.1.2. Weigh approximately 20-30 grams into a labeled, large aluminium weighing tin. Place in hood and air dry for 48 hours or until a constant weight is attained.

6.1.3. Grind and sieve.

6.1.4. Weigh 2.0 grams of air dried soil into a 20 x 150 mm culture tube.

6.1.5. Prepare two additional aliquots of one sample if Quality Control is required.

6.1.6. Prepare a blank and blank spike with 2.0 grams Ottawa sand.

6.1.7. Pipet 100 ul surrogate solution to each culture tube.

6.1.8. Pipet 1000 ul matrix spiking solution to each of the QC culture tubes.

6.1.9. Add 9.9 ml acetonitrile to each sample culture tube and blank and 8.9 mls to QC and blank spike.

6.1.10. Sonicate the samples for 18 hours in a sonic bath packed with ice in the cold room.

6.2. Salting Out

6.2.1. Remove samples from ice bath and allow to come to room temperature.

6.2.2. Transfer 5.0 mls of supernatant to a 16 x 100 mm culture tube.

6.2.3. Add 5.0 ml calcium chloride solution to each sample.

6.2.4. Shake and let stand for 15 minutes.

6.2.5. Centrifuge each sample.

6.2.6. Filter through a 0.45µm PTFE syringe filter into 4 ml **amber** vial, discarding first 3 mls.

6.2.7. Label the extract and deliver to 940.

6.3.8. Complete all paperwork and bench sheet. Bench sheet to include PTFE filter lot #, date and time of transfer to 940 and extract location. Clip the T-card on the folder and place in GC room extraction folder box. The file folder color will be red and the blank name will be ____HOR.SM_.

7. **REFERENCES** - The following USEPA methods are the official methods on which this Laucks Testing Laboratory method is based. The primary methods are those which most closely parallel the Laucks procedure and are referenced by their USEPA series and number. In those instances for which there are no official EPA methods, the most suitable reference is given under the miscellaneous references section. The additional reference section cites those methods which contain additional information. These methods will frequently be official methods, which apply in part to, or support the Laucks method.

PRIMARY REFERENCES:

Test Methods for Evaluating Solid Waste, USEPA, SW-846

8330A (1998)

Kay Zu

EXTRACTIONS BENCH SHEET FORM

LAUCKS TESTING LABORATORIES INC.	EXTRACTION	DATE	METHOD	ANALYST	CHECKER	ANALYSIS
JOB NUMBER: 9908406	8330	8-20-99	8330A	BJD / YL	BJD 8-23-99	8330A
MATRIX: Soil						

Sample #	wt./vol.	1.0 ml	Alig To Rabb	2ND 1.0 ml	To 940		SDG#	Bottle #
9908406-8	2.0 g	10.0 ml	5.0 ml	10.0 ml	~4.0 ml		RF4002	8
8 MS								
8 MSD								
9								9
10								10
11								11
S082099HORS-H2								
B082099HORS-H2								

8-20-99 BJD

COMMENTS:

Start: 1615 for 18 hrs -
Ext + 2nd Time Sol: Acetonitrile - BGJ# B0427
All samples air dried

SURROGATES:

100 ul of: Ex 8-6-6
ul of:

SPIKES:

1000 ul of: Ex 8-3-3
ul of:

STANDARDS:

ul of:
ul of:
ul of:

Fraction and Method	Extraction		Transferred from 921 to 940		Extract Location	Analysis	
8330	Time out 1615	Time in 1630	Time out 1230	Time in —	Transf # 2-111	Time out	Time in
	Date 8-17-99	Initials SP	Date 8-23-99	Initials BJD	D11-E3	Date	Initials
	Time out	Time in	Time out —	Time in 1235		Time out	Time in
	Date	Initials	Date 8-23-99	Initials SO		Date	Initials

Extraction Method for Organochlorine Pesticides and Polychlorinated Biphenyls in Water (8081A/8082 by 3510C)

Method # LTL-3202

December 2, 1999

Revision Number: #2

Written by: _____ Date: 12-2-99

Reviewed by: Harry Romberg Date: 12-13-99

Approved by: Kathy Greps Date: 12-13-99

Controlled Document

No. 20 Assigned to: Tetra

1. **PURPOSE** - In this method, organochlorine pesticides and polychlorinated biphenyls are extracted from neutral water with methylene chloride. The extracts are dehydrated, concentrated in a Kuderna-Danish apparatus and exchanged into hexane. The extract is split prior to any cleanup step. If necessary, the pesticide extract is SPE Florisil cleaned and the PCB extract is acid and SPE Florisil cleaned prior to GC analysis.

2. **SAFETY** - During the conduct of this method, the analyst will be exposed to a variety of reagent chemicals and solvents. The health effects of these various chemicals may be ascertained by reading the material safety data sheets (MSDS) available in the general files. Additionally, the samples by their very nature, may contain significant levels of hazardous materials. It is incumbent on each extractionist to exercise due care and caution while executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **REAGENTS**

3.1. All reagents shall be of AR grade or better.

3.2. All solvents shall be distilled in glass unless otherwise indicated.

3.3. The following special reagents shall be prepared:

3.3.1. 10 N Sodium Hydroxide - weigh 400 grams sodium hydroxide, dissolve and dilute to one liter with DIW.

3.3.2. 1:1 Sulfuric Acid - measure equal volumes of concentrated sulfuric acid and DIW. Note: Observe proper acid preparation techniques.

3.3.3. Anhydrous Sodium Sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400°C.

3.3.4. 9:1 Hexane/Acetone (v/v) - prepared by adding 10.0 ml acetone to 90.0 ml

3.3.5. Florisil SPE column check solution prepared in hexane:

2, 4, 5 - Trichlorophenol	0.100 ug/ml
Gamma BHC	0.020 ug/ml
Heptachlor	0.020 ug/ml
Endrin	0.040 ug/ml
4, 4 - DDD	0.040 ug/ml
4, 4 - DDT	0.040 ug/ml
Methoxychlor	0.200 ug/ml
Alpha BHC	0.020 ug/ml
Dieldrin	0.040 ug/ml
Alpha Endosulfan	0.020 ug/ml
Tetrachloro-m-xylene	0.020 ug/ml
Decachlorobiphenyl	0.040 ug/ml

3.3.6. Surrogate solution prepared in acetone:

2, 4, 5, 6-Tetrachloro-m-xylene	1.0 ug/ml
Decachlorobiphenyl	1.0 ug/ml

3.3.7. Pesticide and/or PCB matrix spiking solution prepared in acetone:

Gamma-BHC	2.5 ug/ml
Heptachlor	2.5 ug/ml
Aldrin	2.5 ug/ml
Arochlor 1260	25.0 ug/ml

4. EQUIPMENT

4.1. Glas-Col machanical separatory funnel shaker

4.2. Organomations Assoc., Inc. - N-EVAP, (Nitrogen Evaporator), Model 112

4.3. Analytichem International - Vac Elut SPS 24 (Vacuum Manifold)

4.4. Vortex mixer

4.5. Standard laboratory glassware to include:

4.5.1. 2000 ml Teflon separatory funnels

4.5.2. 300 ml Fleakers

4.5.3. K-D apparatus: 250 ml. K-D flask, 10 ml or 25 ml ampule and three-ball snyder column.

4.6. All glassware to be rinsed as follows, prior to use:

4.6.1. Technical grade acetone (if the glassware is wet).

4.6.2. Triple rinsed with methylene chloride.

4.7. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

4.8. Florisil SPE cartridges with Teflon frits (500 mg)

5. **QUALITY CONTROL** - The normal level of quality control will consist of blank, blank spikes matrix spike and matrix spike duplicate (MS and MSD). This is performed on a per batch basis to include no more than 20 samples. The level of quality control will be indicated to the extractionist at the time the job is assigned. These samples serve to provide a measure of the recovery efficiency for the analyte and to provide data for statistical evaluation of the sample. In those instances that a client requires additional or different quality control measures, the extractionist will be directed accordingly in writing.

6. **METHODOLOGY**

6.1. Sample Extraction

6.1.1. Mix sample thoroughly in its original container.

6.1.2. Measure 1000 ml sample into a 2000 ml separatory funnel.

6.1.3. Prepare a blank and a blank spike with 1000 ml DIW.

6.1.4. Prepare two additional aliquots of one sample if Quality Control is required.

6.1.5. Pipet 200 ul surrogate solution into each funnel.

6.1.6. Pipet 200 ul matrix spiking solution into each QC funnel.

6.1.7. Adjust pH to 7 ± 2.

6.1.8. Rinse the measuring graduate with methylene chloride and add it to the funnel.

6.1.9. Add 60 ml methylene chloride to the separatory funnel.

6.1.10. Shake the samples hard for three minutes on the mechanical shaker, with the stopcocks closed.

6.1.11. Replace the funnels in rack and allow to stand for 10 minutes.

6.1.12. Drain and collect the lower methylene chloride layer in a fleaker.

6.1.13. Repeat Steps 6.1.9. - 6.1.12. until a total of three extractions have been performed.

6.2. Solvent Dehydration

6.2.1. Prepare a glass funnel by plugging with glass wool, and filling 1/2-2/3 full with sodium sulfate.

6.2.2. Pre-rinse the sodium sulfate by passing 40 ml methylene chloride through the prepared funnel.

6.2.3. Pass the extract from Step 6.1.13. through the funnel and collect in an assembled K-D apparatus.

6.2.4. Rinse the collection vessel with several 10 ml methylene chloride rinses.

6.2.5. Rinse the sodium sulfate with 40 ml of methylene chloride.

6.3. Solvent Evaporation

6.3.1. Assemble the full K-D apparatus with a snyder column prewet with 2-3 ml of methylene chloride.

6.3.2. Immerse K-D apparatus into a hot water bath, using a bath temperature of 90° C, with a long ampule immersed to a depth of 8 ml. Regulate the evaporation time to take one to one and a half hours.

6.3.3. Reduce the volume to 4-5 ml, and exchange into hexane as follows:

6.3.3.1. Add 2-3 ml hexane through the top of the snyder column while the ampule is still immersed in the water bath. Reduce to 4-5 ml.

6.3.3.2. Repeat 6.3.3.1. two additional times.

6.3.4. Remove the apparatus from the water bath and cool to room temperature.

6.3.5. Rinse joint and remove the snyder column. Allow rinse solvent to drain into ampule.

6.3.6. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of hexane.

6.3.7. Reduce the extract volume to less than 2 ml on a nitrogen blowdown. Transfer extract to a 16 x 100 mm culture tube, and adjust to 10.0 ml final volume (as compared to a measured volume) with hexane.

6.4. Sulfuric Acid Cleanup (PCBs only)

6.4.1. Transfer a two ml aliquot from the 10.0 ml final volume (step 6.3.7.) to a 16 x 100 mm culture tube. (Store remaining 8.0 ml of extract.)

6.4.2. Add 2.0 mls concentrated sulfuric acid and vortex for 30 - 60 seconds.

6.4.3. Let stand for a few minutes to allow layers to separate. May be centrifuged.

NOTE: If cleanup is indicated in part of a set of samples, the blank must be split. One portion of the blank should SPE Florisil (Pesticide only), and the other should proceed as 6.5.11.

6.5. SPE Florisil Cleanup (for Pesticides and PCBs)

6.5.1. Attach the vacuum manifold to the vacuum pump with a trap in between. Place a labeled 16 x 100 mm culture tube in the proper collection slot. Secure the manifold with the straps and move the manifold to the waste position. Adjust the vacuum pressure in the manifold to between five and ten pounds of vacuum.

6.5.2. Place one florisil cartridge into the vacuum manifold.

6.5.3. Start the vacuum and prewet the cartridge with hexane/acetone (9:1), by passing at least 5 ml through the cartridge. Do not allow the cartridge to go dry after wetting.

6.5.4. Release the vacuum, and move the manifold to the collect position.

6.5.5. Add 1.0 ml extract from step 6.3.7. (Pesticides) (Store remaining 9.0 ml of extract.) or from step 6.4.3. (PCBs). to the top frit of the florisil cartridge.

6.5.6. Restore the vacuum, and elute the column with 8-9 ml of hexane/acetone (9:1). Allow the cartridge to go dry.

6.5.7. Release the vacuum, and move the manifold to the waste position. Remove and discard the used florisil cartridge.

6.5.8. Repeat from step 6.5.2. for additional extracts.

6.5.9. Reduce the extract volume to 1.0 ml in a warm water bath with nitrogen. Rinse internal walls of ampule several times during blowdown.

6.5.10. Transfer extract to a 1.8 ml vial. The volume is then adjusted to 1.0 ml (as compared to a measured volume) in hexane.

6.5.11. Label the extract and deliver to 940.

6.5.12. Complete all necessary paperwork and bench sheet. Bench sheet to include extract location, time and date of transfer to 940, and if applicable, indicate the SPE Florisil lot number. Clip the T-card on the folder and place in GC room extraction folder box. The file folder color will be purple and the blank name will be ____GPXWL_.

7. **ANALYSIS TIME** - Based on experience in the laboratory, it is anticipated that a single sample may be completed in about six hours. If it is possible to batch similar samples, it is expected that about ten samples could be completed in approximately eighteen hours. About one hour of actual hands on time will be expended by the extractionist if the clean ups are not necessary. These approximate times are based on the assumption that the samples are "average", and will not require significant additional time beyond normal operations. Additional time must be allocated for samples which are very dirty or are extraordinary.

8. **REFERENCES** - The following USEPA methods are the official methods on which this Laucks Testing Laboratory method is based. The primary methods are those which most closely parallel the Laucks procedure and are referenced by their USEPA series and number. In those instances for which there are no official EPA methods, the most suitable reference is given under the miscellaneous references section. The additional reference section cites those methods which contain additional information. These methods will frequently be official methods, which apply in part to, or support the Laucks method.

PRIMARY REFERENCES:

Test Methods for Evaluating Solid Waste, USEPA, SW-846, (1996).

8081A, 8082, 3510C

Extraction Method for Organochlorine Pesticides and Polychlorinated Biphenyls in Soil (8081A/8082 by 3550B)

Method # LTL-3302

November 29, 1999

Revision Number: #2

Written by: _____ Date: 11.29.99

Reviewed by: Harry Romley Date: 12-13-99

Approved by: Kathy Steps Date: 12-13-99

Controlled Document

No. 20 Assigned to: Tetra

1. **PURPOSE** - In this method organochlorine pesticides and polychlorinated biphenyls are extracted from neutral soil with a mixture of methylene chloride and acetone. The extract is dehydrated and concentrated in a Kuderna-Danish (K-D) apparatus. The extract is split prior to any cleanup step. The extracts are GPC and SPF florisil cleaned prior to analysis by GC. The PCBs receive an additional sulfuric acid cleanup.

2. **SAFETY** - During the conduct of this method, the analyst will be exposed to a variety of reagent chemicals and solvents. The health effects of these various chemicals may be ascertained by reading the material safety data sheets (MSDS) available in the general files. Additionally, the samples, by their very nature, may contain significant levels of hazardous materials. It is incumbent on each analyst to exercise due care and caution executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **REAGENTS**

3.1. All reagents are to be AR grade or better.

3.2. All solvents are to be distilled in glass, unless otherwise noted.

3.3. The following special reagents should be prepared:

3.3.1. 1:1 methylene chloride/acetone (v/v)- prepared by mixing equal volumes of the solvents.

3.3.2. 9:1 Hexane/acetone - prepared by adding 10.0 ml acetone to 90.0 ml hexane.

3.3.3. Anhydrous sodium sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400°C.

3.3.4. Florisil SPE column check solution prepared in acetone:

2,4,5-Trichlorophenol	0.100 ug/ml
Gamma BHC	0.020 ug/ml
Heptachlor	0.020 ug/ml
Endrin	0.040 ug/ml
4,4-DDD	0.040 ug/ml
4,4-DDT	0.040 ug/ml
Methoxychlor	0.200 ug/ml
Alpha BHC	0.020 ug/ml
Dieldrin	0.040 ug/ml
Alpha Endosulfan	0.020 ug/ml
Tetrachloro-m-xylene	0.020 ug/ml
Decachlorobiphenyl	0.040 ug/ml

3.3.5. Surrogate solution prepared in acetone:

2,4,5,6-Tetrachloro-m-xylene	1.0 ug/ml
Decachlorobiphenyl	1.0 ug/ml

3.3.6. Pesticide/PCB matrix spiking solution prepared in acetone:

Gamma-BHC	2.5 ug/ml
Heptachlor	2.5 ug/ml
Aldrin	2.5 ug/ml
Arochlor 1260	25.0 ug/ml

4. EQUIPMENT

4.1. Heat Systems Ultrasonic Processer - Model XL2020, 550 watts - Maintain per manufacturer's instructions.

4.1.1. 3/4 inch titanium horn (#208)

4.2. Analytical Biochemical Laboratories, Inc. (ABC) Model 1002B or Model 1000 Gel-Permeation Chromatography (GPC)

4.3. Organomations Assoc., Inc. - N-EVAP (nitrogen evaporator), Model 112

4.4. Analytechem International - Vac Elaut SPS24 (for SPE florisil columns)

4.5. Florisil SPE cartridges with Teflon frits (1000 mg)

4.6. Standard laboratory glassware to include:

4.6.1. 8 ounce extraction bottle

4.6.2. 500 ml Fleakers

4.6.3. K-D apparatus: 500 ml. K-D flask, 10 ml or 25 ml ampule and three-ball snyder column.

4.7. All glassware to be rinsed as follows, prior to use:

4.7.1. Technical grade acetone (if the glassware is wet).

4.7.2. Triple rinsed with methylene chloride.

4.8. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

5. **QUALITY CONTROL** - The normal level of quality control will consist of blanks, blank spikes, matrix spikes and matrix spike duplicates (MS and MSD). This is performed on a per batch basis to include no more than 20 samples. The level of quality control will be indicated to the extractionist at the time the job is assigned. These samples serve to provide a measure of the recovery efficiency for the analyte and to provide data for statistical evaluation of the sample. In those instances that a client requires additional or different quality control measures, the extractionist will be directed accordingly in writing.

6. **METHODOLOGY**

6.1. Sample Extraction

6.1.1. Mix sample thoroughly in its original container if there is space available (otherwise mix in solvent rinsed aluminum tray).

6.1.2. Weigh 30.0 grams of soil (wet weight) into a extraction bottle.

6.1.3. Prepare two additional aliquots of a sample if Quality Control is required.

6.1.4. Add 60 grams sodium sulfate and mix well to give the soil a sandy texture.

6.1.5. Prepare a blank and a blank spike with 60 grams sodium sulfate.

6.1.6. Pipet 200 ul surrogate solution to each bottle.

6.1.7. Pipet 200 ul matrix spiking solution to each of the QC bottles.

6.1.8. Add 100 ml 1:1 methylene chloride/acetone to each bottle.

6.1.9. Sonicate the bottles for 3 minutes using the sonic horn, set at 50% duty cycle and full output (10).

6.1.10. Centrifuge the samples for 20 minutes at 2000 rpm if necessary to achieve a partition.

6.1.11. Decant off and collect the supernatant.

6.1.12. Repeat from steps 6.1.8. two additional times, combining all of the extracts.

6.2. Solvent dehydration

6.2.1. Prepare a glass funnel by plugging with glass wool, and filling 1/2-2/3 full with sodium sulfate.

6.2.2. Pre-rinse the sodium sulfate by passing 40 ml methylene chloride through the prepared funnel.

6.2.3. Pass the extract from step 6.1.12. through the funnel and collect in an assembled K-D apparatus.

6.2.4. Rinse the collection vessel with several 10 ml methylene chloride rinses.

6.2.5. Rinse the sodium sulfate with 40 ml of methylene chloride.

6.3. Solvent evaporation

6.3.1. Assemble the full K-D apparatus with a snyder column prewet with 2-3 ml of methylene chloride.

6.3.2. Immerse K-D apparatus into a hot water bath, using a bath temperature of 90° C, with a long ampule immersed to a depth of 12 ml. Regulate the evaporation time to take one to one and a half hours.

6.3.3. Reduce the volume to 4-5 ml, remove the apparatus from the water bath and cool to room temperature.

6.3.4. Rinse joint and remove snyder column. Allow rinse solvent to drain into ampule.

6.3.5. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of solvent.

6.3.6. Reduce the extract volume to less than 8 ml on a nitrogen blowdown. Transfer extract to a 16 x 100 mm culture tube, and adjust to 10.0 ml intermediate volume (as compared to a measured volume) with methylene chloride.

NOTE: In instances where sample extracts are being prepared for PCB only (8082), and the GPC step is being omitted prior to acid cleanup, the solvent exchange step (see 6.3.8.1.) must be tested. Take 1 ml extract, 1 ml sulfuric acid and vortex. Check for volume changes between layers. If exchange is complete, proceed to 6.4.

6.3.7. At this point the extract will be GPC cleaned -- see Method # LTL-3692.

6.3.8. K-D the GPC cleaned extract to 4-5 ml and exchange into hexane as follows:

6.3.8.1. Add 2-3 ml hexane through the top of the snyder column while the ampule is still immersed in the water bath. Reduce to 4-5 ml.

6.3.8.2. Repeat 6.3.8.1. two additional times.

6.3.9. Remove the apparatus from the water bath and cool to room temperature.

6.3.10. Rinse joint with hexane and remove snyder column. Allow rinse solvent to drain into ampule.

6.3.11. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of hexane.

6.3.12. Reduce the extract to less than four ml in a nitrogen blowdown. Transfer extract to a 16 x 100 mm culture tube and adjust to a final volume of 5.0 ml (as compared to a measured volume) in hexane.

6.4. Sulfuric Acid Cleanup (PCBs only)

6.4.1. Transfer a two ml aliquot from the 5.0 ml final volume (step 6.3.12.) to a 16 x 100 mm culture tube.

6.4.2. Add 2.0 mls concentrated sulfuric acid and vortex for 30 - 60 seconds.

6.4.3. Let stand for a few minutes to allow layers to separate. May be centrifuged.

6.5. Florisil Cleanup

6.5.1. Attach the vacuum manifold to the vacuum pump with a trap in between. Place a labeled 16 x 100 mm culture tube in the proper collection slot. Secure the manifold with the straps and move the manifold to the waste position. Adjust the vacuum pressure in the manifold to between five and ten pounds of pressure.

6.5.2. Place one florisil cartridge into the vacuum manifold.

6.5.3. Start the vacuum and prewet the cartridge with hexane/acetone (9:1), by passing at least 5 ml through the cartridge. Do not allow the cartridge to go dry after wetting.

6.5.4. Release the vacuum, and move the manifold to the collect position.

6.5.5. Add 1.0 ml extract from step 6.3.12. (Pesticides) or from step 6.4.3. (PCBs). to the top frit of the florisil cartridge. (Store remaining 4.0/3.0 ml of extract.)

6.5.6. Restore the vacuum, and elute the column with 8-9 ml of hexane/acetone (9:1). Allow the cartridge to go dry.

6.5.7. Release the vacuum, and move the manifold to the waste position. Remove and discard the used florisil cartridge.

6.5.8. Repeat from step 6.5.2. for additional extracts.

6.5.9. Reduce the extract volume to 1.0 ml in a warm water bath with nitrogen. Rinse internal walls of culture tube several times during blowdown.

6.5.10. Transfer extract to a 1.8 ml vial. The volume is then adjusted to 1.0 ml (as compared to a measured volume) in hexane.

6.5.11. Label the extract and deliver to 940.

6.5.12. Complete all necessary paperwork and bench sheet. Bench sheet to include the date of GPC, florisil lot number, date and time of transfer to 940 and extract location. Clip the T-card on the folder and place in the GC room extraction folder box. The file folder color will be purple and the blank name will be ____GPX.SL_.

7. **ANALYSIS TIME** - Based on experience in the laboratory, it is anticipated that a single sample may be completed in about 12 hours. If it is possible to batch similar samples it is expected that about seven samples could be completed in approximately 20 working hours. About four and a half hours of hands on time will be required of the extractionist. These approximations are based on the assumption that the samples are "average", and will not require additional time beyond normal operations. Additional time must be allocated for samples which are very dirty or are extraordinary, such as tissues or vegetable matter.

8. **REFERENCES** - The following USEPA methods are the official methods on which this Laucks Testing Laboratory method is based. The primary methods are those which most closely parallel the Laucks procedure and are referenced by their USEPA series and number. In those instances for which there are no official EPA methods, the most suitable reference is given under the miscellaneous references section. The additional reference section cites those methods which contain additional information. These methods will frequently be official methods, which apply in part to, or support the Laucks method.

PRIMARY REFERENCES:

Test Methods for Evaluating Solid Waste, USEPA, SW-846, (1996).

8081A, 8082, 3550B.

Extraction Method for Polynuclear Aromatics in Soil
(8270C by 3550B)

Method # LTL-3450

November 29, 1999

Revision Number: #1

Written by: B. O Quill Date: 11-29-99

Reviewed by: Harry Romberg Date: 12-13-99

Approved by: Kathy Oreps Date: 12-13-99

Controlled Document

No. 20 Assigned to: Tetra

1. **PURPOSE** - In this method, polynuclear aromatics are extracted from neutral soils with a mixture of methylene chloride and acetone. The extract is dehydrated, concentrated in a Kuderna-Danish (K-D) apparatus and alumina cleaned prior to analysis by GC Mass Spectrometer. This method also includes low concentration (SIM).

2. **SAFETY** - During the conduct of this method, the analyst will be exposed to a number of reagent chemicals and solvents. The health effects of these various chemicals may be ascertained by reading the material safety data sheets (MSDS) available in the general files. Additionally, the samples, by their very nature may contain significant levels of hazardous materials. It is incumbent on each analyst to exercise due care and caution executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **REAGENTS**

3.1. All reagents are to be AR grade or better.

3.2. All solvents are to be distilled in glass, unless otherwise noted.

3.3. The following special reagents should be prepared:

3.3.1. 1:1 methylene chloride/acetone (v/v)- prepared by mixing equal volumes of the solvents.

3.3.2. Anhydrous sodium sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400°C.

3.3.3. Alumina, Neutral, Brockman Activity I - activate 60-325 mesh alumina by heating for 16 hours at 130° C.

3.3.4. Surrogate solution prepared in methanol:

1-Fluoronaphthalene	250 ug/ml
Fluorene-d10	250 ug/ml
Pyrene-d10	250 ug/ml

Low Concentration (SIM) surrogate solution prepared in methanol:

1-Fluoronaphthalene	5.0 ug/ml
Fluorene-d10	5.0 ug/ml
Pyrene-d10	5.0 ug/ml

3.3.5. Matrix spiking solution and Low Concentration (SIM) matrix spiking solution prepared in methanol:

Acenaphthene	50 ug/ml
Acenaphthylene	50 ug/ml
Anthracene	50 ug/ml

Benzo(a)anthracene	50 ug/ml
Benzo(a)pyrene	50 ug/ml
Benzo(b)fluoranthene	50 ug/ml
Benzo(ghi)perylene	50 ug/ml
Benzo(k)fluoranthene	50 ug/ml
Chrysene	50 ug/ml
Dibenzo(a,h)anthracene	50 ug/ml
Fluoranthene	50 ug/ml
Fluorene	50 ug/ml
Indeno(1,2,3-cd)pyrene	50 ug/ml
Naphthalene	50 ug/ml
Phenanthrene	50 ug/ml
Pyrene	50 ug/ml
2-Methylnaphthalene	50 ug/ml

4. EQUIPMENT

4.1. Heat Systems Ultrasonic Processor - Model XL2020, 550 watts - Maintain per manufacturer's instructions.

4.1.1. 3/4 inch titanium horn (#208).

4.2. Organomations Assoc., Inc. - N-EVAP, (nitrogen evaporator), Model 112

4.3. Standard laboratory glassware to include:

4.3.1. 8 ounce extraction bottles

4.3.2. 500 ml Fleakers

4.3.3. K-D apparatus: 500 ml. K-D flask, 10 ml or 25 ml ampule and three-ball snyder column.

4.4. All glassware to be rinsed as follows, prior to use:

4.4.1. Technical grade acetone (if the glassware is wet).

4.4.2. Triple rinsed with methylene chloride.

4.5. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

4.6. Teflon thistle tubes

4.7. Disposable Monstr-pette (large pasteur pipets)

5. **QUALITY CONTROL** - The normal level of quality control will consist of blanks, blank spikes, matrix spikes and matrix spike duplicates (MS and MSD). This is performed on a per batch basis to include no more than 20 samples. The level of quality control will be indicated to the extractionist at the time the job is assigned. These samples serve to provide a measure of the recovery efficiency for the analyte and to provide data for statistical evaluation of the sample. In those instances that a client requires additional or different quality control measures, the extractionist will be directed accordingly in writing.

6. **METHODOLOGY**

6.1. Sample Extraction:

6.1.1. Mix sample thoroughly in its original container if there is space available (otherwise mix in solvent rinsed aluminum tray).

6.1.2. Weigh 30.0 grams of soil (wet weight) into an extraction bottle.

6.1.3. Prepare two additional aliquots of a sample if Quality Control is required.

6.1.4. Add 30 to 60 grams sodium sulfate and mix well to give the soil a sandy texture.

6.1.5. Prepare a blank and a blank spike with 60 grams sodium sulfate.

6.1.6. Pipet 200 ul surrogate solution to each bottle.
(Low Conc.: 500 ul of low conc. surrogate solution.)

6.1.7. Pipet 500 ul matrix spiking solution to each of the QC bottles.
(Low Conc.: 50 ul of matrix spiking solution.)

6.1.8. Add 100 ml 1:1 methylene chloride/acetone to each bottle.

6.1.9. Sonicate the bottles for 3 minutes using the sonic horn, set at 50% duty cycle and full output (10).

6.1.10. Centrifuge the samples for 20 minutes at 2000 rpm if necessary to achieve a partition.

6.1.11. Decant off and collect the supernatant.

6.1.12. Repeat from step 6.1.8. two additional times, combining all of the extracts.

6.2. Solvent dehydration

6.2.1. Prepare a glass funnel by plugging with glass wool, and filling 1/2-2/3 full with sodium sulfate.

6.2.2. Pre-rinse the sodium sulfate by passing 40 ml methylene chloride through the prepared funnel.

6.2.3. Pass the extract from step 6.1.12. through the funnel and collect in an assembled K-D apparatus.

6.2.4. Rinse the collection vessel with several 10 ml methylene chloride rinses.

6.2.5. Rinse the sodium sulfate with 40 ml of methylene chloride.

6.3. Solvent Evaporation

6.3.1. Assemble the full K-D apparatus with a snyder column prewet with 2-3 ml of methylene chloride.

6.3.2. Immerse K-D apparatus into a hot water bath, using a bath temperature of 90° C, with a long ampule immersed to a depth of 12 ml. Regulate the evaporation time to take one to one and a half hours.

6.3.3. Reduce the volume to 4-5 ml and remove the apparatus from the water bath. Cool to room temperature.

6.3.4. Rinse joint and remove snyder column. Allow rinse solvent to drain into ampule.

6.3.5. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of solvent.

6.3.6. Reduce the extract to 1.0 ml in a warm water bath with nitrogen. Rinse internal walls of ampule several times during blowdown.

6.4. Alumina Cleanup

6.4.1. Prepare a Monstr-pette column by plugging with a small amount of glass wool.

6.4.2. Pack column with a minimum of 3 gm. of activated alumina. Top with 1/2 cm of sodium sulfate.

6.4.3. Attach Teflon thistle tube and pre-elute column with 10 ml methylene chloride.

6.4.4. Add extract directly to top of the sodium sulfate and allow to elute onto the column.

6.4.5. Rinse the ampule twice with a small amount of methylene chloride and add to top of column.

6.4.6. Re-attach the Teflon thistle tube to the column and add a minimum of 10 ml methylene chloride

6.4.7. Elute into a 16 x 125 mm culture tube.

6.4.8. Reduce the extract volume to 1.0 ml in a warm water bath with nitrogen. Rinse internal walls of the culture tube several times during blowdown.

6.4.9. Transfer extract to a 1:8 ml vial. The final volume is then adjusted to 1.0 ml (as compared to a measured volume) in methylene chloride. (Low Conc.: Final volume adjusted to 1.0 ml. in methylene chloride.)

6.4.10. Label the extract and deliver to 940.

6.4.11. Complete all paperwork and bench sheet. Bench sheet to include alumina lot #, the date of transfer to 940 and extract location. Clip the T-Card on the ~~folder~~ and place in GC/MS room extraction folder box. The file folder color will be blue and the blank name will be ____MPN.SL_.

7. **ANALYSIS TIME** - Based on extensive experience in the laboratory, it is anticipated that a single sample may be completed in about ten hours. If it is possible to batch similar samples, it is expected that about six samples could be completed in approximately 16 hours. About one and one half hours of hands on extractionist time will be required per sample. These approximations are based on the assumption that the samples are "average", and will not require additional time beyond normal operations.

8. **REFERENCES** - The following USEPA methods are the official methods on which this Laucks Testing Laboratory method is based. The primary methods are those which most closely parallel the Laucks procedure and are referenced by their USEPA series and number. In those instances for which there are no official EPA methods, the most suitable reference is given under the miscellaneous references section. The additional reference section cites those methods which contain additional information. These methods will frequently be official methods, which apply in part to, or support the Laucks method.

PRIMARY REFERENCES:

Test Methods for Evaluating Solid Waste, USEPA, SW-846.

8270C (1996), 3550B (1996), 3610B (1996)

Extraction Method for Chlorinated Herbicide in Water
(8151A by 3510C)

Method # LTL-3510

November 15, 1999

Revision Number: #7

Written by: B. O'Neill Date: 11-15-99

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Approved by: Kathy Kreps Date: 11-23-99

Controlled Document

No. 20 Assigned to: Tetra

1. **PURPOSE** - In this method the samples are extracted with diethyl ether, then esterified with diazomethane for analysis by GC/ECD.

2. **SAFETY** - During the conduct of this method, the analyst will be exposed to a variety of reagent chemicals and solvents. The health effects of these various chemicals may be ascertained by reading the material safety data sheets (MSDS) available in the general files. Additionally, the samples, by their very nature, may contain significant levels of hazardous materials. It is incumbent on each analyst to exercise due care and caution executing this method. The company will provide any protective equipment or clothing needed to assure employee safety.

3. **MATERIALS**

3.1. All reagents are to be AR grade or better.

3.2. All solvents are to be distilled in glass unless otherwise noted.

3.3 The following special reagents should be prepared:

3.3.1. 10 N Sodium Hydroxide - weigh 400 grams sodium hydroxide, dissolve and dilute to one liter with DIW.

3.3.2. 12 N Sulfuric Acid - measure 334 mls of concentrated sulfuric acid and dilute to one liter with DIW. Note: Observe proper acid preparation techniques.

3.3.3. 10% Hydrochloric Acid - measure 100 ml concentrated hydrochloric acid and dilute to one liter with DIW. Note: Observe proper acid preparation techniques.

3.3.4. Anhydrous Sodium Sulfate - prepared by muffling AR grade sodium sulfate for four hours at 400°C.

3.3.5. Acidified Sodium Sulfate - Weigh the anhydrous sodium sulfate (see 2.3.2.) in 100 gram increments into a suction flask. Cover the sodium sulfate with ethyl ether containing 0.1 ml concentrated sulfuric acid for each 100 g increment. Swirl the slurry for about two minutes then stopper the flask and apply an aspirator vacuum until the ether is removed . Place on a steam bath in a hood to assure that all ether is removed. Store in a closed bottle.

3.3.6. 10 M Potassium Hydroxide - prepared by dissolving 56.1 grams potassium hydroxide pellets and diluting to 100 ml with DIW.

3.3.7. Diazald® (Aldrich Chemical Co., Milwaukee, WI - catalog no. D2,800-0).

3.3.8. Silicic Acid - Activate and store at 130° C.

3.3.9. Surrogate solution prepared in methanol:

2,6-Dichlorobenzoic Acid	4.0 ug/ml
2,4-Dichlorophenyl Acetic Acid	8.0 ug/ml

3.3.10. Matrix Spiking solution prepared in methanol:

Pentachlorophenol	0.4 ug/ml
Picloram	2.0 ug/ml
2,4,5-TP	2.0 ug/ml
2,4,5-T	2.0 ug/ml
Dicamba	2.0 ug/ml
Dinoseb	4.0 ug/ml
2,4-DB	4.0 ug/ml
2,4-D	4.0 ug/ml
Dalapon	4.0 ug/ml
Dichloroprop	4.0 ug/ml
4-Nitrophenol	4.0 ug/ml
MCPP	200.0 ug/ml
MCPA	200.0 ug/ml

4. EQUIPMENT

4.1. Glas-Col mechanical separatory funnel shaker

4.2. Organomations Assoc., Inc. - N-EVAP, (nitrogen evaporator), Model 112

4.3. Standard laboratory glassware to include:

4.3.1. 2000 ml Teflon separatory funnels

4.3.2. 300 ml Fleakers

4.3.3. 1000 ml Erlenmeyer flask

4.3.4. K-D apparatus: 250 ml. K-D flask, 10 ml or 25 ml ampule and three-ball snyder column

4.4. All glassware to be used shall be rinsed in the following manner:

4.4.1. 10% hydrochloric acid

4.4.1. Technical grade acetone

4.4.2. Triple rinsed with methylene chloride

4.5. Acid washed glass wool

4.6. Volumetric measurements are to be made with a calibrated fixed or adjustable volume microdispenser and individually calibrated vials.

5. **QUALITY CONTROL** - The normal level of quality control will consist of blank, blank spike, matrix spike and matrix spike duplicate (MS and MSD). This is performed on a per batch basis to include no more than 20 samples. The level of quality control will be indicated to the extractionist at the time the job is assigned. These samples serve to provide a measure of the recovery efficiency for the analyte and to provide data for statistical evaluation of the sample. In those instances that a client requires additional or different quality control measures, the extractionist will be directed accordingly in writing.

6. **METHODOLOGY**

6.1. Sample Extraction:

6.1.1. Mix sample thoroughly in its original container.

6.1.2. Measure 1000 ml sample into a graduated cylinder.

6.1.3. Quantitatively transfer sample to a 2000 ml separatory funnel.

6.1.4. Prepare a blank and blank spike with 1000 ml DIW.

6.1.5. Prepare two additional aliquots of a sample if Quality Control is required.

6.1.6. Pipet 250 ul surrogate solution into each funnel.

6.1.7. Pipet 250 ul matrix spiking solution into each QC funnel.

6.1.8. Add 250 gram of sodium chloride. Let set until dissolved.

6.1.9. Adjust pH to >12 with approx. 13 mls of 10 N sodium hydroxide. Let set for 1-2 hours, shaking periodically.

6.1.10. Add 60 ml methylene chloride to each separatory funnel.

6.1.11. Shake hard for three minutes on the mechanical shaker, with the stopcocks closed.

6.1.12. Replace the funnels in rack and allow to stand for 10 minutes.

6.1.13. Drain and discard the lower methylene chloride.

6.1.14. Repeat steps 6.1.10.-6.1.13. until a total of three extractions have been performed.

6.1.15. Adjust pH to <2 with approx. 17 mls of cold (4° C) 12 N sulfuric acid.

6.1.16. Add 120 mls ethyl ether to each separatory funnel.

6.1.17. Shake the samples for three minutes on the mechanical shaker, with the stopcocks open.

6.1.18. With stopcocks closed, replace the funnels in rack and allow to stand for 10 minutes.

6.1.19. Drain and collect the lower aqueous phase into a 1000 ml flask.

6.1.20. Collect the ether layer in a 300 ml Fleaker containing approx. 10 grams acidified sodium sulfate. Transfer the aqueous layer back into the separatory funnel, rinsing with ethyl ether.

6.1.21. Add 60 mls ethyl ether and repeat steps 6.1.17.-6.1.20. until a total of three extractions have been performed.

6.1.22. Allow extract to remain in contact with the acidified sodium sulfate for a minimum of 2 hours, periodically swirling the extract and sodium sulfate. If sodium sulfate is not free flowing, add a few additional grams. Extract may be stored overnight.

6.2. Extract Concentration

6.2.1. Transfer the extract from step 6.1.22. to an assembled K-D apparatus through acid washed glass wool, rinsing with small amounts of ethyl ether.

6.2.2. Assemble the full K-D apparatus with a snyder column prewet with 2-3 ml of ethyl ether.

6.2.3. Immerse K-D apparatus into a hot water bath, using a bath temperature of 60-65°C, with a short ampule immersed to a depth of 10 ml.

6.2.4. Reduce the volume to approx. 3 mls and remove the apparatus from the water bath. Allow to cool to room temperature. (Concentration should be completed in 10 - 20 minutes.)

6.2.5. Rinse joint with ethyl ether and remove the snyder column. Allow rinse solvent to drain into ampule.

6.2.6. Remove the ampule clamp, and wipe the joint with a Kimwipe. Separate the ampule and rinse the joint with a small amount of ethyl ether.

6.2.7. Transfer the extract to a 16 x 100 mm culture tube, rinsing the ampule with ethyl ether.

6.2.8. Reduce volume to 1.0 ml in nitrogen blowdown, immersed in a warm water bath.

6.2.9. Add 1.0 ml iso-octane and bring to 4.0 ml with ethyl ether.

6.3. Derivatization:

6.3.1. Prepare a derivatization standard by adding 250 ul surrogate solution and 250 ul matrix spiking solution to 4.0 ml ethyl ether/iso-octane (see step 6.2.9.) in a 16 x 100 culture tube.

6.3.2. To tube A (the first tube in the train), add 1 ml methanol and approx. 8.0 ml with ethyl ether.

6.3.3. To tube B add:

6.3.3.1. 2.0 ml 10 M potassium hydroxide

6.3.3.2. 1.4 ml Carbitol (diethylene glycol monoethyl ether)

6.3.4. Place 10 ul micro-pipet in each sample tube from step 6.2.9.

6.3.5. Connect nitrogen line to the apparatus and regulate so that tube A bubbles actively but not violently.

6.3.6. Add 2 scoops (approximately 0.1-0.2 grams) of Diazald and 1.4 ml ethyl ether to tube B. Stopper.

6.3.7. Bubble the generated diazomethane into the tube for 90 seconds. (Extract will turn bright yellow.)

6.3.8. Let extract stand for 20 minutes.

6.3.9. Add 0.1 - 0.2 gm. activated silicic acid to each culture tube. Allow to stand until evolution of nitrogen gas has stopped. This may take a couple of hours and may be stored overnight.

6.3.10. Adjust the final volume to 10.0 ml (as compared to a measured volume) with hexane.

6.3.11. Label the extract and deliver to 940.

6.3.12. Complete all the necessary paperwork and bench sheet. Bench sheet to include time and date of transfer to 940 and extract location. Clip the T-card on the folder and place in the GC room extraction folder box. The file folder color will be yellow, and the blank name will be ____GHB.WL_.

7. **ANALYSIS TIME** - Based on experience in the laboratory, it is anticipated that a single sample may be completed in about 16-18 hours. If it is possible to batch similar samples it is expected that about five samples could be completed in approximately 18-20 hours. About five hours of hands on time will be required of the analyst. These approximations are based the assumption that the samples are "average", and will not require significant additional time beyond normal operations. Additional time must be allocated for samples which are very dirty or are extraordinary.

8. **REFERENCES** - The following USEPA methods are the official methods on which this Laucks Testing Laboratory method is based. The primary methods are those which most closely parallel the Laucks procedure and are referenced by their USEPA series and number. In those instances for which there are no official EPA methods, the most suitable reference is given under the miscellaneous references section. The additional reference section cites those methods which contain additional information. These methods will frequently be official methods, which apply in part to, or support the Laucks method.

PRIMARY REFERENCES:

Test Methods for Evaluating Solid Waste, USEPA, SW-846

8151A (1996), 3510C (1996)

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-4002

Title: **Electronic Sample Entry and Log-In**

Revision history:

Number	Date
6	3/18/99
5	6/19/96
4	12/28/95
3	4/05/95
2	6/05/90
1	4/24/90

Revised by: Pam Johnson
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Date: 3-25-99

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Date: 3-25-99

Controlled Document

No. 20 **Assigned to:** TETRA

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1. INTRODUCTION AND SCOPE

1.1 Introduction

1.1.1 This procedure is a description of sample receipt, sample log-in, and sample tracking when samples are logged into the laboratory's Laboratory Information Management System (LIMS). The collection of programs and procedures which comprise the LIMS is called "SAM." References made to SAM in this SOP are references to this collection of programs and procedures.

1.1.2 Sample entry must be performed in a timely fashion to allow tests with short holding times to be started immediately. Accuracy in the recording of sample IDs, in marking samples with lab numbers, and in checking for consistency of all records is of utmost importance.

1.2 Scope

1.2.1 All samples received by the laboratory are logged using the following procedures.

2. EQUIPMENT LIST

Lab coat
Disposable gloves
Respirator, dust mask
3M desk cleaner, broom, dustpan, mop
Spatula
Waterproof labeling gun
PC work station linked to SAM

3. SAFETY PRECAUTIONS

3.1 Sample Handling

3.1.1 Samples received at the laboratory can potentially be contaminated with toxic materials. Reasonable caution must be exercised at all times when handling these samples. Such precautions include wearing a lab coat at all times, using gloves, using a hood (located in Inorganics) to perform operations when necessary (strong odors present, etc.), and wearing a respirator or dust mask if fumes or dust are generated.

3.1.2 Cleanliness and neatness are of utmost importance. All spills and condensation from wet sample containers must be cleaned up immediately. This will help to alleviate accidental sample breakage and protect others from possible contact with contaminated work areas.

3.1.3 When wearing gloves, be certain to remove them when opening the cooler or lab doors and when answering the phone. The gloves which protect the sample enterer from contamination may transfer contamination to these objects. Other persons may touch the door knob or phone without glove protection and have the contamination transferred to their unprotected hands. Never put pens, paper clips, etc. in your mouth.

3.1.4 A dust mask is worn when pouring dry packing material such as vermiculite into the garbage.

4. OPERATION PROCEDURES

4.1 Sample Receipt

4.1.1 Samples may be received by client delivery, over the front counter, via UPS, courier services, by various air freight and overnight delivery services, and by Greyhound. It is the responsibility of the sample enterer to ensure that samples received by any of these services are promptly logged in and work requests made to the laboratory.

4.1.2 If a chain-of-custody (COC) is received with the sample set, sign it and record the date and time it was received. If the client has delivered the samples by hand, verify the cooler contents and return a copy of the COC to the client.

4.1.3 If complete verification of the cooler contents will occur later, then the COC is stamped and the stamped copy returned to the client. This stamp is reproduced in Appendix 1. Verification must take place within one working day of receipt.

4.1.4 All discrepancies between the COC and the actual samples received are immediately reported to the client and are noted on the Sample Receipt Log. CLP Sample Receipt Log (Appendix 3) is for CLP log-in procedure. **NON-CLP** Sample Receipt Log (Appendix 2) is for Laucks **NON-CLP** log-in procedure. If requested a client provided receipt form may be substituted for the Laucks sample receipt log.

4.1.5 Put on gloves, open the coolers (in the hood if necessary), and note whether custody seals are present and, if so, intact. **Affix one of the intact custody seals on the sample receipt log.** If there is a question about the integrity of the custody seals, make a note on the CLP Sample Receipt Log (Appendix 3); the client must be informed.

4.1.6 After the coolers are opened, determine whether there are soil or water samples in the coolers. Typically there will be a number of sample bottles for each sample if they are water; soils will have only a small number of containers per sample.

4.1.7 Visually check the contents of the opened cooler for obvious damage or broken sample containers. Note any breakage on the appropriate Sample Receipt Log.

4.1.8 For any program (such as HAZWRAP, NFESC, or Army Corps) or other project-related samples either the enclosed temperature blank or at least 3 separate containers taken randomly from different locations in EACH cooler must be checked for temperature with the infrared thermometer. The temperatures are recorded on the Supplemental Sample Receipt Log (Appendix 3). If any samples exceed the range of 4°C ± 2°C, the client must be contacted. In most cases, this should be done **in writing** (preferably FAX) by the appropriate project manager. A copy of the communication from the Supplemental Sample Receipt Log must be kept with the COC in the work order file.

4.1.9 Remove all bottles from the cooler and put on the bench. Line up the bottles in some kind of order, if there is an apparent order. Various means of ordering samples are:

- COC order
- Client sample ID
- Date sampled
- Time sampled

4.1.10 For samples consisting of multiple containers, place all containers together on the bench.

4.1.11 After all samples are arranged then check consistency between the COC and the sample labels for Sample IDs, dates and times on each sample container.

4.1.12 Determine whether custody seals are present on the individual sample containers (jars and bottles). If present and intact, so note. If present and any seal is broken, so note. These notations must be made on the CLP Sample Receipt Log Form (Appendix 3).

4.1.13 All preserved water sample bottles for project-related work as well as unpreserved water sample bottles for HAZWRAP, NFESC, or Army Corps projects must also be checked for pH at the time of sample receipt. This is done by pouring out some of the sample into a small plastic cup and then using pH paper to record the pH at time of receipt. Volatiles samples should **NOT** be checked. When better discrimination of pH is needed, narrow range pH paper should be used to confirm the pH (especially if the pH is within 1 pH unit of the required preservation limit for that sample). All pH measurements must be recorded on the Supplemental Sample Receipt Log (Appendix 3). If any samples exceed the pH requirements, the client must be contacted. In most cases, this should be done **in writing** (preferably FAX) by the appropriate project manager. The samples with inappropriate pH are listed on Laucks Testing Lab pH log form (Appendix 5) for corrective action. After the corrected preservation is completed this form is given to the appropriate project manager for work order filing.

4.1.14 Some samples are received at the lab that need to be split and preserved for different analytes. To accommodate preservation requirements, these samples are recorded on the "Sample Split Sheet" (see Appendix 6). There is a specific cart located in sample entry where the samples are temporarily stored until splitting and preservation take place.

4.1.15 All sample container marks (including ID's, dates and times) are then verified with each other and with the COC. This is done by noting whether all bottles from the same sample have the same ID and whether this ID is the same as on the COC. All discrepancies are noted on the Non-CLP Sample Receipt Log (Appendix 2) or the CLP Sample Receipt Log (Appendix 3) and reported to the client.

4.1.16 To determine if the sample(s) is(are) acceptable, compare the existing conditions with the criteria specified in Appendix 7, "Required Containers/Volumes, Preservation Techniques and Maximum Holding Times for Environmental Analysis". All listed criteria must be met in order to qualify the sample(s) as "acceptable". If there are any problems with the sample(s) these must be documented in the "CLP Sample Receipt Log" (see Appendix 3). If any samples are not acceptable, the client must be contacted. In most cases, this should be done **in writing** (preferably FAX) by the appropriate project manager.

4.2 Sample Log-In

4.2.1 Determine whether a client record exists in the SAM database. If it does not, create a record. At a minimum, the client record will include:

- an alphanumeric client code (up to 12 digits)
- the client's full and accurate name, address, and point of contact
- the client's telephone number and/or FAX number
- the full and complete address for invoices
- the purchase order/contract number <u>if</u> that number applies to <u>all</u> work the client may submit. (If the purchase order/contract number is specific to one sample submittal, by project etc.), then the client code would be project specific. Example (client name_project name).

4.2.2 A SAM work order is started for the job through the ORD program. The work order is identified by a unique 7-digit number which is assigned by SAM at the time the work order is initiated. (The first two digits of this number represent the year, the third and fourth digits represent the month, and the final three digits represent the work order's sequence within the month. For instance, work order 9004001 was initiated in April,

1990 and was the first work order for that month.) This number will be used throughout the laboratory to track the job.

```
Laucks Testing   ORDER INFORMATION   01/13/94 11:42:21
9401499
 KEYS    ST   ORDER # 94-01-496                          RECEIVED 01/12/94      SAMPS
9401485 WR                                               DATE DUE 01/26/94        2
9401486 TR    CLIENT 1_LH_NIECE      INVOICE BY R        VER BY
9401487 TR   PROJECT                  % DISCOUNT         KEEP FOR  45
9401488 WR   CONTACT KARIS           TEST/JOB            KEEP TIL 03/12/94      DP/TST
9401489 TR       CAT 1436759          % SURCHARGE            DISP D
9401490 TR                           #REP/INV  3   3
9401491 WR                                               QUOTED $               MS    4
9401492 WR   COMPANY L.H. Niece & Co.                    SAMPLE $ UNKNOWN
9401493 TR     FACIL Vashon, WA. 98070                     MISC $
9401494 WR                                               TOTAL $ UNKNOWN
9401495 TR       REP Larry Niece                           INV #
9401496 WR     PHONE (206)463-5281
9401497 WR                                                CREATED 01/13/94
9401498 TR   WORK ID Wesleyan Community Church            WRITTEN 01/13/94
9401499 WR     TAKEN Client                             TRANSMIT
9401500 WR     TRANS UPS                                COMPLETE
9401501 WR      TYPE Water                              REPORTED
9401502 WR     ATTEN Larry Niece                        INVOICED
              P.O. #                                 WRITTEN BY PAMJ
                                                                          CL NL SL J1
F1 | F2 | F3 | F4 | F5 | F6 | F7 | F8 | F9 | F10 | HELP
```

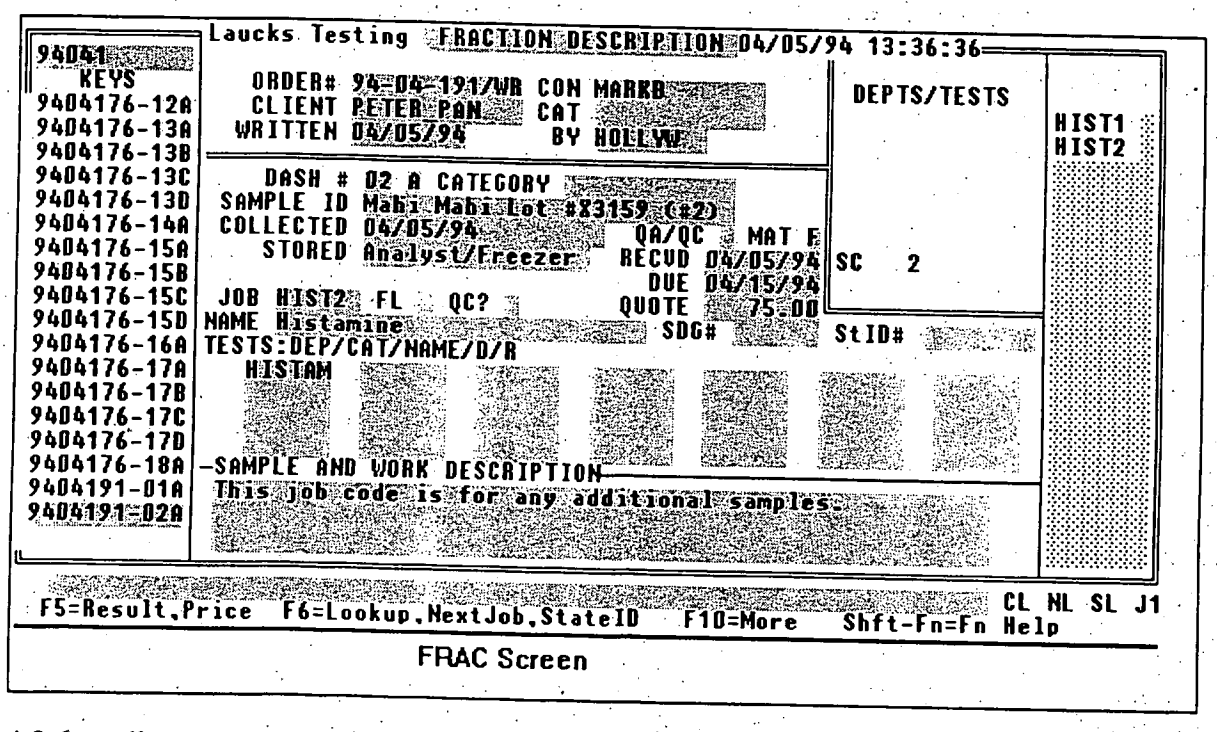
ORD Screen

4.2.3 The work order is to be filled out as completely as possible at this time. Above is an example of what the work order screen looks like on your PC. Typical information put into the work order screen (analogous to a cover page) includes:

- date of sample receipt;
- work order due date;
- client point of contact (if different than in the client record);
- sample type (soil, water, etc.);
- the manner in which the samples were received at the laboratory (hand-delivered, Greyhound, etc.);
- air bill number (or equivalent) if the sample was transported by common carrier;
- the client's overall project identification (both the name of the project and any project, job, or purchase order number);
- and any relevant surcharges or discounts to be applied at the time of invoice.

4.2.4 All required data entry fields are in inverse video (highlighted) on the screen, but fields for purchase order numbers, project name or number, and point of contact should also be completed, if the information is known.

4.2.5 All sample IDs, dates of collection, and dates of receipt are recorded in the FRAC program for the work order with which they are associated. If there is a discrepancy in identification between bottles of the same sample, make a note on the appropriate sample receipt log and the project manager will notify the client.



FRAC Screen

4.2.6 All sample bottles are numbered with the work order number and a fraction (or sample) number. Fraction numbers are assigned sequentially to each sample based on the order in which the samples were sorted and logged (COC order, client sample number order, etc.). This number is used to track the sample throughout the laboratory. See section 4.2.10 for specifications for unique bottle identifiers required by Navy projects.

4.2.7 A sample can be uniquely identified by its work order number and the fraction number. For instance, if the work order number was 9004001 and there were 4 samples, the job would consist of samples

9004001-01
9004001-02
9004001-03
9004001-04

4.2.8 Each sample or set of samples is assigned a unique identifying work order number, generated by the Laboratory Information Management System (LIMS), on receipt. This unique number consists of 7 numerical characters, such as 9007215. In this example, the work order was initiated in 1990 (90), in the month of July (07) and was the 215th such work order that month (215). If more than 999 workorders are generated in any month, the 5th digit is replaced by successive letters of the alphabet (A-Z).

4.2.9 If necessary, more than one fraction may be created for a sample (generally, this is related to billing issues - when one analysis is discounted in price and another is not, for instance), but they will all bear the same fraction number and be differentiated by an automatically-assigned letter suffix. For instance, if sample 9004001-01 had 3 fractions, purely for internal accounting reasons, the three fractions would be identified as:

9004001-01A
9004001-01B
9004001-01C

4.2.10 The person performing log-in needs to be aware of this effect, but it has no impact on sample identification within the lab, on sample tracking, or on the sample number placed on the bottles/jars. In the above example, all bottles submitted for this sample would be marked 9004001-01.

4.2.11 For Navy projects, each bottle must have a unique bottle identifier. Every bottle must have a specific 1-3 digit numerical identifier that is unique to each bottle submitted within a workorder. The numbers are assigned in consecutive order so that all bottles of similar size/type with the same preservation for the same analysis (analyses) from a particular workorder will have consecutive bottle numbers. The first bottle of each analysis type in each new workorder starts over again with bottle number 1.

4.2.12 This information must be recorded in the "Bottles" computer tracking program under each workorder and the workorder-unique bottle identifier will be printed in the bottom left corner of each bottle label (which also contains the workorder number and the sample number) before the bottle label is affixed to each individual bottle.

4.2.13 **ALERT:** Each SAM work order can accommodate up to 57 fractions and no more. Each work order must allow sufficient fraction space for later changes or additions. Therefore, no more than 50 samples should be logged into any single work order. If, for administrative reasons, some or all of the samples consist of more than one fraction, then no more than 50 <u>fractions</u> can be logged. Should the submittal consist of more than 50 samples, or more than 50 fractions, initiate additional work orders as required. Cross-reference the work order numbers, so that all samples submitted together can be reported

together to the client. You can perform this cross-reference manually (by noting on accompanying documents "See Also [Work Order Number]) or you can make appropriate comments in the Work Order Comment field (F2). To the degree possible, make sure that multiple work orders which represent one complete project in the client's mind are created sequentially, with no other unrelated work order numbers intervening.

4.2.14 Additionally, Sample **D**elivery **G**roups (SDGs) are commonly created for project work at the time of sample entry. SDGs consist of no more than 20 samples being analyzed for the **same** test. This is in order that the appropriate amount of QC may be analyzed and reported with any sample set. Specifics of the SDG creation process are outlined elsewhere in this SOP.

4.2.15 **ALERT:** Each fraction will accommodate only 27 tests. If more than 27 analyses are required on any sample, additional fractions should be made (i.e. -1A, -1B, -1C, etc.).

4.2.16 **ALERT:** The work order will accommodate only one date of receipt, while each fraction will accommodate individual receipt dates and due dates. If samples are submitted over several days, and are logged into one work order, the Sample Custodian **MUST** enter appropriate dates of receipt in each fraction. The FRAC program will default to the current date. If the samples were received on an earlier date, that date **MUST** be entered for that fraction for the date to be correct. Similarly, the fraction due date will default to that of the workorder on the ORD screen. If different fractions of the same sample are due at different times, due to client or other demands, the date they are due **MUST** be entered for that fraction.

4.3 Special documentation procedures for CLP samples

4.3.1 Completion of the CLP Sample Receipt Log, and the Supplemental Sample Receipt Log

4.3.2 CLP Sample Receipt Log and the Supplemental Sample Receipt Log are CLP-specific sample login sheets. For each cooler received a CLP Sample Receipt Log Form and a Supplemental Sample Receipt Log must be completed. This form takes the place of the NON-CLP Sample Receipt Log (Appendix 2). Copies of these forms may be found in Appendix 3.

4.3.3 Complete the header information requested at the top of the forms. Use multiple pages if necessary.

- date received
- time received
- client name
- SDG #
- COC # (if available)
- sample log-in date
- work order #
- client project
- airbill number (if available)
- and initials of the person logging in the samples.

4.3.4 Complete the Non-Conformance check list. If there is a problem with the custody seals, chain of custody records, or agreement between the custody records, the client must be contacted. In this case, this should be done **in writing** (preferably FAX) by the appropriate project manager. A copy of the communication must be kept with the COC in the work order file.

4.3.5 Since the extractable fractions will be transferred to the extractions lab, a Secure Storage Custody Log must be completed, and the samples are held on 8C in the WO1 walk-in cooler (extractions hold shelf) pending pick-up by extractions personnel. Specifics of the Storage Custody Log is outlined in the Chain-Of-Custody SOP located in the SOP manual.

4.4 Assignment of SDG numbers

4.4.1 The SDG name is assigned by sample control and is usually based on client name or project name followed by sequential numbering.

4.5 Assignment of lab quality control samples

4.5.1 The client may choose to designate which samples are to be analyzed as matrix spike/matrix spike duplicate samples. This means that the sample preparations and the VOA departments cannot self-assign QC samples until all samples from the SDG are received. It is the responsibility of the sample login person to notify the operations staff when a specified QC sample is received.

4.5.2 Note in the **SAM SDG** records which sample is QC-assigned.

4.5.2.1 This information is pulled into SDG from the FRAC program when the SDG is created.

4.5.2.2 On the FRACTION screen, an X is placed in the QC field. This will print out next to the sample and indicate that it is an assigned QC sample.

4.5.2.3 Write a department comments message for whichever department (EX, MS, and/or GC) should be notified.

4.6 Completion of SDG records.

4.6.1 For each project (NFESC, HAZWRAP, or Army Corps) SDG records in SAM are created. The SDG concept follows the CLP model: that is, up to 20 samples of similar matrix and analytical fraction are grouped together for preparation and analysis. Samples are assigned to SDGs at sample login and are also reported by SDG.

4.6.2 The **SDG** program is an electronic means of compiling information about the samples assigned to an SDG in one place. Example **SDG** screens are reproduced on the following page:

```
CDM                    SDG Database
  KEYS   SDG Group : CDM10        Date Due: 03/13/93        Created:  02/19/93
BOGO5G   Fraction  : E SPUMITO                              Updated:  02/19/93
BOGO5I   Project   : CDM (EDB)                 Client:
BOGO6G   SAS Number:                Case Number:                Max. Samps:
BOGO6I
BOGO7G    Work  Samp                                                Associated
BOGO7I    Ord   Num  QC                Client ID          Mat TS pH    Blank
BRPTSS
CANONS   9302598 17   *  07-MW-005-0-000-F                W
CB2SFV   9302598 20      07-MW-007-0-000-F                W
CB3-3V
CBSFXS
CDM10E
CDM10G
CDM10I
CDM10P
CDM10S
CDM10V
CDM11E
CDM11G
5=Lookup,Copy,Print  6=Toggle    F10=More    Shft-Fn=Fn Help                CL NL SL J1
```

SDG, Screen 1

```
CDM                 SDG Database
  KEYS   SDG Group : CDM10        Date Due: 03/13/93        Created:  02/19/93
BOGO5G   Fraction  : E SPUMITO                            Updated:  02/19/93
BOGO5I   Project   : CDM (EDB)                 Client:
BOGO6G   SAS Number:                  Case Number:              Max. Samps:
BOGO6I
BOGO7G     Work   Samp                  Date
BOGO7I     Ord    Num    VTSR        Collected
BRPTSS
CANONS   9302598  17  02/16/93  02/13/93
CB2SFU   9302598  20  02/16/93  02/13/93
CB3-3U
CBSFXS
CDM10E
CDM10G
CDM10I
CDM10P
CDM10S
CDM10U
CDM11E
CDM11G
                                                                  CL NL SL J1
5=Lookup,Copy,Print  6=Toggle     F10=More   Shft-Fn=Fn Help
```

SDG, Screen 2

```
CDM                 SDG Database
  KEYS   SDG Group : CDM10        Date Due: 03/13/93        Created:  02/19/93
BOGO5G   Fraction  : E SPUMITO                            Updated:  02/19/93
BOGO5I   Project   : CDM (EDB)                 Client:
BOGO6G   SAS Number:                  Case Number:              Max. Samps:
BOGO6I                                          Fractions
BOGO7G     Work   Samp
BOGO7I     Ord    Num    EDB
BRPTSS
CANONS   9302598  17     X
CB2SFU   9302598  20     X
CB3-3U
CBSFXS
CDM10E
CDM10G
CDM10I
CDM10P
CDM10S
CDM10U
CDM11E
CDM11G
                                                                  CL NL SL J1
5=Lookup,Copy,Print  6=Toggle     F10=More   Shft-Fn=Fn Help
```

SDG, Screen 3

```
CDM                 SDG Database
  KEYS   SDG Group : CDM10        Date Due: 03/13/93        Created:  02/19/93
BOGD5G   Fraction  : E SPVMITO                              Updated:  02/19/93
BOGD5I   Project   : CDM (EDB)                 Client:
BOGD6G   SAS Number:                Case Number:          Max. Samps:
BOGD6I
BOGD7G
BOGD7I
BRPTSS
CANONS
CB2SFV
CB3-3V   Comments:
CBSFXS
CDM10E
CDM10G
CDM10I
CDM10P
CDM10S
CDM10V
CDM11E
CDM11G
                                                          CL NL SL J1
5=Lookup,Copy,Print  6=Toggle     F10=More    Shft-Fn=Fn Help
```

SDG, Screen 4

4.6.3 Fill in the header section of the first screen page. For CLP cases, fill in the Fraction (V=Volatiles, P=Pesticides, S=Semivolatiles etc..) Indicate the project name, and the client's name.

4.6.4 When the work order number and sample number are entered, the sample-specific information shown in screens 1, 2, and 3 is read in from the SAM database. (**Hint**: after the first work order number is entered, it is only necessary to enter sample numbers for subsequent samples from the same work order.)

4.6.5 On screen 3, a table of fractions/tests is created. An 'X' is entered to signify that a particular test is required on a given sample.

4.6.6 Each 'fraction' has a separate SDG entry. For instance, VOAs and ABNs are entered on separate SDG records, as indicated above (V=Volatiles, S=Semivolatiles, P=Pesticides). A single letter suffix (V, S, P etc...) is assigned to each SDG record before it is saved to disk. The end result is that you may have multiple SDG records for a given SDG, each with the same root name, but a different suffix. This system is used to allow for the possibility that within the same SDG, varying numbers of tests will be assigned to samples within that SDG.

4.6.7 The last screen page is used for any comments which the sample login person or project manager would like to record for the operations staff.

4.7 Sample storage

4.7.1 The following tests must be started very soon after receipt when performed on water samples.

Test Type/Name	SAM Code(s)
NO_3 - nitrate	NO3ICW
NO_2 - nitrite	NO2_W, NO2_DW
ortho phosphate and soluble reactive phosphate	P04O_W, P04S_W
Cr^{+6} - hexavalent chromium	CR6_W, CR6_WM
CO_2 - carbon dioxide	CO2_N
DO - dissolved oxygen	DO_W
BOD - Biological Oxygen Demand	BOD_5
Chlor A - Chlorophyll A	CHLORA
Settleable Solids	SETSOL, SETSL2
Filtration for dissolved metals	FILTER
pH	PH_EPW, PH_SWW
Microbiological tests	[various]
Color	COL_DW
Turbidity	TUR_TW, TUR_W
Sulfite	SO3_W
MBAS - Methylene Blue Active Substances	MBAS
Chlorine	CL2_R

4.7.2 A rush backlog report is printed throughout the day for short holding-time tests, with the exception of microbiology, in order that they be recognized by the analysts. **A checklist (Appendix 8) for analyses with short holding times is completed prior to release of samples to the laboratory. Sample management will verify that the correct RUSH test codes are entered, date, time received and collected dates are accurate and to ensure matrices and sample I.D.s are correct at time of log-in.**

4.7.3 For microbiological samples and for samples which arrive late in the day and for which the holding time will expire if the analysis is not started that day, the containers must be taken immediately to the work areas in which the tests will be performed and the primary person responsible for these tests notified that samples are here. A list with the name of the appropriate analyst is posted in the sample entering area.

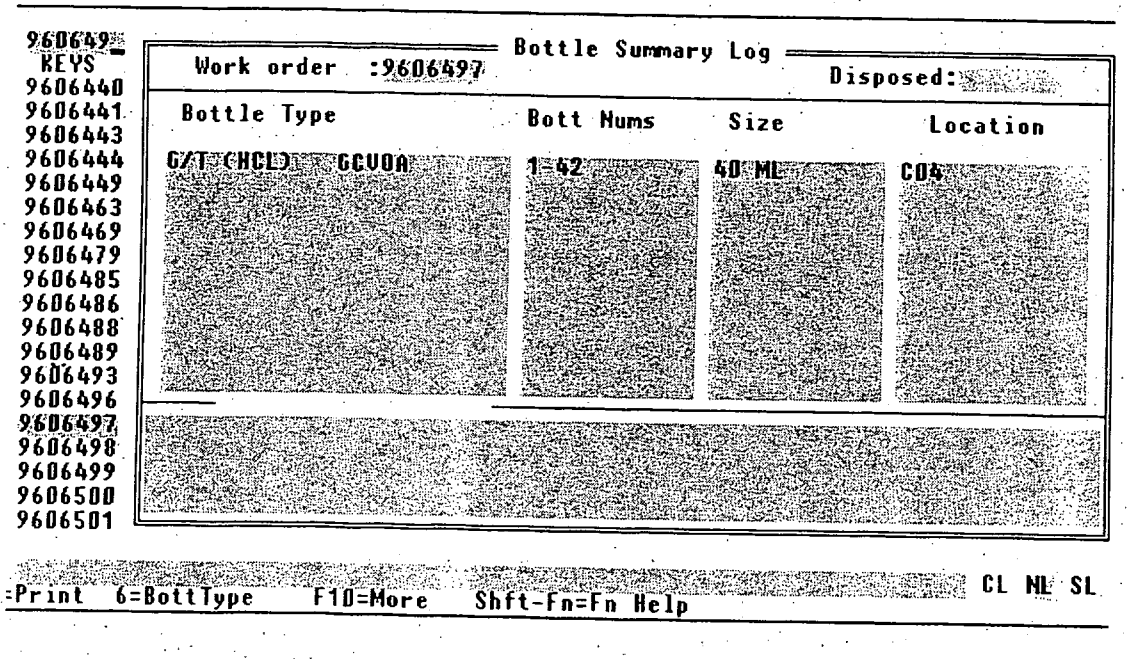
4.8 Storage locations

Location	Description of contents
VOA refrigerator	Soil and water volatiles
Shelf	Aqueous metals, oils, no cooling required
Inorganics cooler	Complete small water jobs
Walk-in cooler	All other soil and water*
Section in the walk-in cooler indicated w/CLP sign-in, sign-out sheets	All samples that are under internal COC. CLP samples are also stored in here.

4.8.1 *See Section 4.7 for transfer of extractable aliquots to the extractions lab

4.8.2 Prior to putting bottles into any storage location, the electronic Bottle Summary Log must be completed. For Navy projects, unique bottle identifiers must also be entered in the bottle log.

4.8.3 At the J1 prompt, type "BOTTLES." This log details how many bottles were received, what type and size of bottles were received, the storage location of the bottles and the bottle numbers, where applicable. An example of this log follows.



4.9 Determination of tests

4.9.1 If Laucks provided sample bottles for the client, the bottle order, the client COC, file notes, letters, client instructions, or the client file are consulted as necessary to determine what tests are to be performed. The type of bottles received for water samples will help greatly in determining which tests to perform. If you can't determine the tests, give the paperwork to the Project Manager, who will contact the client.

4.9.2 A lab work request is initiated at this time. Based on a review of the above information, test codes are assigned to the appropriate fractions. These test codes may represent single-data point analyses ("regular" tests) or multiple-data point analyses ("special" tests), such as GC/MS volatiles. However, no work request packet can be prepared until after "transmittal," which is initiated by the Project Manager or designee.

4.9.3 Some soil samples will need to be shared between two or more departments. In order of priority, the following areas will receive samples in this order:

4.9.4 If volatiles are requested, then the VOA departments will get the samples first (GC or GC/MS)

4.9.5 The sample/samples will then be sent to the extractions lab

4.9.6 The extractions lab will return the sample/samples to the inorganics lab or other areas

4.9.7 At the time of sample log-in the Sample Custodian will make appropriate comments for the department to return the samples to other departments for further testing. **Before** any samples are sent to other departments for testing, it is imperative that any requiring the analysis of volatile organics gets the sample first. Such samples should be given to the Volatiles Department before any other department.

4.10 Electronic Transmittal of Sample and Test Request Records

4.10.1 Specifics of the transmittal process are detailed in a separate SOP. A brief summary follows. For actual transmittal, that SOP should be referenced as it will detail greater specifics and will contain changes that may occur in the transmittal process. The following is only intended as a brief overview and may not reflect the most current practices.

4.10.2 All documentation (including, but not limited to, air bills, chain-of-custody documents, bottle order forms, notes, contracts, messages, letters, etc.) that supports the information entered into the work order and the sample fractions is clipped together by the Sample Custodian when sample log-in is complete. The work order number is written on, at a

minimum, the chain-of-custody document and may also be written on any other relevant documents.

4.10.3 The supporting documentation is given to the project manager, her designee, or to the head of the Project Management Group for "transmittal." Transmittal is the electronic approval of the work order and sample fractions as written and must be performed within 1 working day of sample log-in. Transmittal is the activity which electronically puts the samples and test requests into the laboratory's analytical schedule.

4.10.4 In performing the transmittal, it is the responsibility of the Project Manager, or designee, to double-check the work order and test fractions for the following:

- accuracy of project information (number, name, point of contact, etc.)
- accuracy of test requests
- and accuracy of the test codes employed to represent those test requests.

4.10.5 The Project Manager makes corrections to these items as necessary, usually in consultation with the Sample Custodian. When transmittal is complete, the hard-copy record generated in the transmittal process is stapled to the supporting documentation previously assembled by the Sample Custodian and the complete record is filed alphabetically (by client name) in the filing drawer designated. If a CLP-style package is being generated, packets are prepared for the CLP Document Control Custodian.

4.10.6 Specific test requests are made known to analysts through hard-copy work "backlogs". For a description of this process, see the SOP on Data Handling.

4.11 Generation of internal Chain-of-Custody (COC)

4.11.1 Samples which must be removed from the main building at 940 and taken to the extractions lab at 921 for preparation are tracked with an internal COC. This form is initiated by the person logging in the samples. The lab number, the client name, the number of samples, the sample matrixes and the enterer's initials and the date and time the form is started are recorded. See Appendix 4 for an example of an internal COC.

4.11.2 The samples are placed on shelf 8C in the walk-in with the COC. The person removing the samples from 940 signs and dates the form. The samples are logged into a log book at 921 before being placed in the cooler.

4.11.3 The COC is returned to 940 with the extracts when extractions are completed.

4.12 Sample breakage

4.12.1 All sample breakage, whether in shipping or while handling in the lab, must be reported immediately to the Project Manager.

4.12.2 If the sample was water, clean thoroughly with disposable towels. Be very careful with broken glass so as to avoid cuts.

4.12.3 If the sample was soil, as much of the sample as possible is transferred to a new, clean jar using a spatula. Be certain not to pick up any sample which has contacted the floor. Save the original label, if possible. Note on the log-in records that the sample was broken and transferred to a new container.

4.12.4 All dirty, disposable clean up materials, soil, broken glass, etc. are placed in a plastic garbage bag before being placed in the dumpster. Any non-disposable clean up materials are washed after use.

4.13 Special circumstances

4.13.1 Samples from some clients are logged into a monthly work order. Some jobs extending over more than one sampling event may be entered under one work order number. In that event, pay special attention to date of receipt (see ALERT, above).

4.13.2 Other special circumstances may arise. If there are any questions, check with the Project Manager first.

APPENDIX 1

Sample Receipt Verification Stamp

Sample Receipt acknowledged pending verification of sample count. You will be notified within one working day of any discrepancies found

Signed _____ Date _____ Time _____

APPENDIX 2

NON-CLP Sample Receipt Log

Laucks Testing Laboratories, Inc.
NON-CLP SAMPLE RECEIPT LOG

Initial once samples are checked in_____

DATE RECEIVED:_____
TIME RECEIVED:_____
CLIENT NAME:_____
SDG #_____
COC #_____

SAMPLE LOG-IN DATE:_____
WORKORDER #:_____
CLIENT PROJECT:_____
AIRBILL ATTACHED?:(#)_____
RECEIVED BY:_____

Non-Conformance: (Check applicable item(s)) Client IDs affected:

°(1) Not enough sample sent for proper analysis. #s affected:_____
☐(2) Sample Bottle received broken and/or cap not intact._____
☐(3) Custody seal: Absent____ Present/Intact_____ Present/Broken _____
☐(4) Any temperature out of compliance:_____
☐(5) Sample received outside of holding time._____
☐(6) Sample not properly preserved. pH = ___. Wrong preservative used._____
☐(7) Illegible sample numbers or label missing from bottles._____
☐(8) Identification on bottle same as identification on paperwork: yes:_____no:_____
☐(9) Incomplete instructions received with sample(s), i.e.,
☐ no Request for Analysis, no Chain-of-Custody._____
☐(10) Samples received in improper container._____
☐(11) Samples held in field before receipt by Lab. Days (specify)_____
☐(12) Air Bubble(s) in ___of ____ samples for volatiles analysis._____
☐(13) Other _____

CORRECTIVE ACTION: (Check applicable item(s)
Correction action taken by:

	Inititals	Date
☐(1) Client informed verbally (Client Services).	_____	
☐(2) Client informed by memo/letter/fax (Client Services).	_____	____
☐(3) Sample processed "as received" (Sample Entry).	_____	____
☐(4) Re-sampling requested of client (Client Services).	_____	____
☐(5) Samples placed "on hold" until further notice (Sample Entry/Client Services).	_____	____
☐(6) NOTE IN NARRATIVE. See temperature/pH login sheet. (Sample Entry).	_____	____
☐(7) Other (Specify)_____	_____	____

* When complete (within 24 hours of nonconformance) forward to QA. Original to be forwarded to initiator to be included in transmittal file.

Comments:

APPENDIX 3

CLP Sample Receipt Log

Supplemental Sample Receipt Log

COOLER RECEIPT FORM

WORKORDER #: _____

Contractor Cooler _____
QA Lab Cooler # _____
Number of Coolers _____

Project: _____

Date samples were received at the laboratory: ___/___/___

A. PRELIMINARY EXAMINATION PHASE: Date cooler was opened: ___/___/___

By: (print)_____(sign)_____

1. Did cooler come with a shipping slip (airbill, etc.),>>>>>>>>>>>>>>>>>>>>> YES NO
   If YES, record carrier name and airbill number: _____
2. Were custody seals on outside of cooler?>>>>>>>>>>>>>>>>>>>>>>>>>>>> YES NO
   How many and where: _____
   Seal date: ___/___/___Seal name: _____
3. Were custody seals unbroken and intact at the date and time of arrival?>>>>>> YES NO
4. Did you screen samples for radioactivity using the Geiger Counter?>>>>>>>> YES NO
5. Were custody papers sealed in a plastic bag and taped inside to the lid?>>>>>> YES NO
6. Were custody papers filled out properly (ink, signed, etc.)?>>>>>>>>>>>>>>> YES NO
7. Did you sign custody papers in the appropriate place?>>>>>>>>>>>>>>>>>>>YES NO
8. Was project identifiable from custody papers? If YES, enter project name at top of this form.
9. If required, was enough cooling material present?>>>>Type of ice: _____YES NO
10. Have designated person initial here to acknowledge receipt of cooler: ____date___/___/___

B. LOG-IN PHASE : Date samples were logged-in: ___/___/___

By (print)._____(sign)_____

11. Describe type of packing in cooler: _____
12. Were all bottles sealed in separate plastic bags?>>>>>>>>>>>>>>>>>>>>>> YES NO
13. Did all bottles arrive unbroken and were labels in good condition?>>>>>>>> YES NO

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LAUCKS TESTING LABORATORIES, INC.
COOLER RECEIPT FORM (continued)

14. Were all bottle labels complete (ID, date, time signature, preservative, etc.)? YES NO
15. Did all bottle labels agree with custody papers?>>>>>>>>>>>>>>>>>>>>>>>>YES NO
16. Were correct containers used for the tests indicated?>>>>>>>>>>>>>>>>>>>>YES NO
17. Were correct preservatives added to samples?>>>>>>>>>>>>>>>>>>>>>>>>>YES NO
18. Was a sufficient amount of sample sent for tests indicated?>>>>>>>>>>>>>> YES NO
19. Were bubbles absent in VOA samples: If NO, list by QA #:>>>>>>>>>>>>> YES NO
20. Was project manager called / faxed & status discussed? >>>>>>>>>>>>>>>>> YES NO
    If YES, give details below
21. Who was called / faxed? _____
    By whom?_____(date)_____

DISCREPANCIES:

_____
_____
_____
_____
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_____

Page 2 of 3

Laucks Testing Laboratories, Inc., Supplemental Sample Receipt Log

Work Order Number:_____
Assigned SDG Number:_____

Temperature		pH of Bottle Types								

Allowable temperature and pH ranges (neutral pH defined as a value between 5 and 9)

Temperature	Allowable temperature range is 4± 2 degrees Celsius
Acid Preserved pH	pH must be less than 2
Base Preserved pH	pH must be greater than 12

APPENDIX 4

Secure Storage Custody Log

Organic Extractions Custody Log

Laucks Testing Laboratories, Inc.

Secure Storage Custody Log

Project:_____ **LTL Number:**_____

Number of Containers (*optional*):_____

Storage Unit:_____ **SDG Number** (*optional*):_____

Sample Numbers	Matrix (*optional*)	Location (*shelf*)	Logged Out		By	Logged In		By	Action
			Date	Time		Date	Time		

Samples Disposed of by _____ on _____

Laucks Testing Laboratories, Inc.

Organic Extractions Custondy Log

Samples Entered By	Time	Date	JOB #	
			Client	
Samples Moved From Bldg. 940 to 921 by:			*Matrix*	*Sample #*
			SOIL	
			WATER	
			SLUDGE	
			MISC.	
			OIL	

Comments:

APPENDIX 5

Laucks Testing Lab pH Log Form

Laucks Testing Lab pH log Form

Date_____

Analyst	WO Number	Fractions	pH before	Volume Acid Added/Type	Resulting pH

APPENDIX 6

Laucks Testing Lab Sample Split Sheet

Laucks Testing Lab Sample Split Sheet

WO #	Sample #	WE HAVE	WE NEED	TOTAL	DISS	UNPRES	INTL & DATE	BOTTLE TYPES
								Y = YELLOW
								B = BLUE
								C = CYANIDE
								R = RED
								O = O&G
								P = PHENOL
								S = SULFIDE
								T = TOC
								OTHER

APPENDIX 7

Required Containers/Volumes/Preservation/Holding Times

REQUIRED CONTAINERS/VOLUMES, PRESERVATION TECHNIQUES AND MAXIMUM HOLDING TIMES FOR ENVIRONMENTAL ANALYSIS

A. PRIORITY POLLUTANTS - Organics Analysis (Federal Register Vol. 49, No. 209, October, 1984)

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Purgeable Halocarbons	2 - 40 ml containers	Glass, Teflon-lined Septum, 40 ml capacity	Cool, 4° C, no headspace	14 days, with preservation	Method 601, GC/ELCD or Method 624, GC/MS
Purgeable Aromatic Hydrocarbons	2 - 40 ml containers	Glass, Teflon-lined Septum, 40 ml capacity	Cool, 4° C, adjust pH to $\leq$ 2 HCl, no headspace	14 days, with preservation 7 days, if not preserved	Method 602, GC/PID or Method 624, GC/MS
Acrolein and Acrylonitrile	2 - 40 ml containers	Glass, Teflon-lined Septum, 40 ml capacity	Cool, 4° C, if there is presence of residual chlorine then preserve with 0.5 g ascorbic acid, no headspace As above, and pH adjusted to pH 4-5.	7 days 14 days	Method 624, GC/MS
Phenols	1 liter	Glass, Teflon-lined Septum, 1 liter or 1 gallon capacity	Cool, 4° C, if there is presence of residual chlorine then preserve with 0.008% $Na_2S_2O_3$ pH <2 H_2SO_4.	7 days until extraction; 40 days after extraction for analysis	Method 625, GC/MS

A. PRIORITY POLLUTANTS - Organics Analysis (Federal Register Vol. 49, No. 209, October, 1984) (continued)

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Pesticides (Organochlorine Pesticides, and PCB's	1 liter	Glass, Teflon-lined Septum, 1 liter or 1 gallon capacity	Cool, 4° C	7 days until extraction; 40 days after extraction for analysis	Method 608, GC
Polynuclear Aromatic Hydrocarbons (PAHs)	1 liter	Glass, Teflon-lined Septum, 1 liter or 1 gallon capacity	Cool, 4° C	7 days until extraction; 40 days after extraction for analysis	Method 610, GC or Method 625, GC/MS
Base/Neutral and Acid Extractables	1 liter	Glass, Teflon-lined Septum, 1 liter or 1 gallon capacity	Cool, 4° C	7 days until extraction; 40 days after extraction for analysis	Method 625, GC/MS

B. WASTE EVALUATION - ORGANICS ANALYSIS (SW-846, 3rd Edition)

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Halogenated Volatile Organics	2 - 40 ml containers for liquids 20 grams for solids	Glass, Teflon-lined Septum, 40 ml capacity Above or Glass, 2-4 oz. capacity	Cool, 4° C, no headspace Cool, 4° C, packed to avoid headspace	14 days 14 days	Method 8010 GC/Hall - Direct Injection or Headspace, Method 5020 Purge-and-Trap, Method 5030 or Method 8260/Method 8240, GC/MS Purge-and-Trap Method 5030
Nonhalogenated Volatile Organics	2 - 40 ml containers for liquids 20 grams for solids	Glass, Teflon-lined Septum, 40 ml capacity Above or Glass, 2-4 oz. capacity	Cool, 4° C, adjust pH $\leq$ 2 with HCl, no headspace Cool, 4° C, packed to avoid headspace	14 days, with preservation 7 days, if not preserved 14 days	Method 8015 GC/FID Direct Injection or Headspace, Method 5020 Purge-and-Trap, Method 5030 or Method 8260/Method 8240, GC/MS Purge-and-Trap Method 5030

B. WASTE EVALUATION - ORGANICS ANALYSIS (SW-846, 3rd Edition) (continued)

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Aromatic Volatile Organics	2 - 40 ml containers for liquids 20 grams for solids	Glass, Teflon-lined Septum, 40 ml capacity Above or Glass, 2-4 oz. capacity	Cool, 4° C, if there is presence of residual chlorine then preserve with 0.5 g ascorbic acid and adjust pH to ≤2 with HCl, no headspace Cool, 4° C	14 days with preservation 14 days	Method 8020, GC/PID Direct Injection or Headspace, Method 5020 - Purge-and-Trap, Method 5030 Method 8260/8240, GC/MS Purge-and-Trap Method
Acrolein, Acrylonitrile Acetonitrile	2 - 40 ml containers for liquids 20 grams for solids	Glass, Teflon-lined Septum, 40 ml capacity Above or Glass, 2-4 oz. capacity	Cool, 4° C, adjust pH 4-5 with HCl, no headspace Cool 4° C, no headspace	14 days, with preservation 14 days	Method 8030, GC/FID Direct Injection or Headspace, Method 5020 - Purge-and-Trap Method 5030 - Groundwater using Method 5030 only. Method 8260/8240, GC/MS Purge-and-Trap Method
Phenols	Approximately 1 liter for liquid sample Approximately 50 grams for sludge or solid sample	Glass, Teflon-lined cap	Cool, 4° C, 35 mg $Na_2S_2O_3$ per ppm free chlorine per liter, adjust pH <2 with H_2SO_4 Cool 4° C	Extracted within 7 days and completely analyzed within 40 days Extracted within 14 days and completely analyzed within 40 days	Method 8040 GC/FID or GC/ECD or Method 8270 GC/MS
Organochlorine Pesticides and PCBs	Approximately 1 liter for liquid sample Approximately 50 grams for sludge or solid sample	Glass, Teflon-lined cap	Cool, 4° C, adjust pH to 6-8 with H_2SO_4 or NaOH Cool, 4° C	Extracted within 7 days and completely analyzed within 40 days Extracted within 14 days and completely analyzed within 40 days	Method 8080 GC/ECD

B. WASTE EVALUATION - ORGANICS ANALYSIS (SW-846, 3rd Edition) (continued)

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Polynuclear Aromatic Hydrocarbons (PAHs)	Approximately 1 liter for liquid sample Approximately 50 grams for sludge or solid sample	Glass, Teflon-lined cap	Cool, 4° C	Extracted within 7 days and completely analyzed within 40 days Extracted within 14 days and completely analyzed within 40 days	Method 8310 HPLC or Method 8270 GC/MS
Chlorinated Hydrocarbons	Approximately 1 liter for liquid sample Approximately 50 grams for sludge or solid sample	Glass, Teflon-lined cap	Cool, 4° C	Extracted within 7 days and completely analyzed within 40 days Extracted within 14 days and completely analyzed within 40 days	Method 8270 GC/MS
Organo-phosphorus Pesticides	Approximately 1 liter for liquid sample Approximately 50 grams for sludge or solid sample	Glass, Teflon-lined cap	Cool, 4° C	Extracted within 7 days and completely analyzed within 40 days 14 days	Method 8140 GC/NPD or GC/NPD/ECD
Chlorinated Herbicides (i.e., 2,4-D and 2,4,5-TP)	Approximately 1 liter for liquid sample Approximately 50 grams for sludge or solid sample	Glass, Teflon-lined cap	Cool, 4° C	Extracted within 7 days and completely analyzed within 40 days Extracted within 14 days and completely analyzed within 40 days	Method 8150 Extraction and Esterification/GC-ECD

B. WASTE EVALUATION - ORGANICS ANALYSIS (SW-846, 3rd Edition) (continued)

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Volatile Organics (VOAs)	2- 40 ml containers for liquid sample 20 grams for solids	Glass, Teflon-lined Septum 40 ml capacity As above or glass, 2-4 oz.	Cool, 4° C, acid preserved with HCl to pH < 2, no headspace Cool, 4° C, no headspace or if solid packed to minimize headspace	14 days 14 days	Method 8260 Purge-and-Trap GC/MS
Semi-Volatile Organics	Approximately 1 liter for liquid sample Approximately 50 grams for sludge or solid sample	Glass, Teflon-lined cap	Cool, 4° C,	Extracted within 7 days and completely analyzed within 40 days Extracted within 14 days and completely analyzed within 40 days	Method 8270 GC/MS

C. WASTE EVALUATION - GENERAL

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Toxicity Characteristic Leaching Procedure	Approximately 1 liter for liquid sample Approximately 200 grams for solid sample	Glass, Teflon-lined cap	VOA, Metals, Semivolatiles, Pesticides/Herbicides - 14 days until extraction. Follow analytical protocol for aqueous holding time or holding time from leachate preparation.	Not specified	According to requested analysis
Water Reactivity	Approximately 100 ml for liquid sample Approximately 50 grams for solid sample	-----	None	14 day	-----

C. WASTE EVALUATION - GENERAL (continued)

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Ignitability	Approximately 200 ml or 50 grams	None specified	None	14 days	Method 1010 Pensky-Martens Closed-Cup Method Method 1020 Setaflash Closed Cup Method
Corrosivity	100 - 500 ml	Plastic	None	None	Method 1110 Corrosivity Toward Steel
California Assessment Manual CAM/STLC	Approximately 200 ml for liquid sample Approximately 10 grams for solid sample	Plastic or Glass	No preservation for solid sample. Add HNO_3 to pH <2 for liquid sample	28 days for Mercury 6 months for others	See Methods for Metals Analysis

D. METALS ANALYSIS (EPA Methods for Chemical Analysis of Water and Wastes, March 1983, or APHA Standard Methods, 15 Edition. and EPA SW-846, 3rd Edition)

PARAMETER	MINIMUM VOLUME REQUIRED **	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Mercury, Total/Dissolved Mercury, Total	100-200 ml for liquid sample Approximately 5 grams for solid sample	Plastic or Glass	HNO_3 to pH <2 for total Filter on site, HNO_3 to pH <2 for dissolved	28 days	EPA 245.1 for water or EPA 7470A EPA 7471A for sediment Cold Vapor Method
Metals, Total Metals, Dissolved	300 ml for liquid samples Approximately 10 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 for total Filter on site, HNO_3 to pH <2 for dissolved	6 months	Flame AA-- See Individual Metal Methods Emission AA-- See Individual Metal Methods Graphite Furnace AA- See individual Metal Methods or ICP-- 200.7 or 6010

**** For individual metals the aggregate minimum volume is determined by the number of discrete analytical methods not the sum of all the individual analytes.**

D. METALS ANALYSIS (EPA Methods for Chemical Analysis of Water and Wastes, March 1983, or APHA Standard Methods, 15 Edition. and EPA SW-846, 3rd Edition) (continued)

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Hexavalent Chromium -Cr^6	200 ml for liquid sample Approximately 50 grams for solid samples	Plastic or Glass	Cool, 4 C	24 hours Extracted within 7 days, analyzed within 24 hrs. of extraction.	EPA 218.4 or EPA 7196A EPA 218.5 or EPA 7197 Extraction/AA Method EPA 7196 Colorimetric Method
Aluminum (Al)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 202.1, Flame EPA 202.2 or EPA 7020, Furnace
Antimony (Sb)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 204.1 or EPA 7040, Flame EPA 204.2 or EPA 7041, Furnace
Arsenic (As)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 206.3 or EPA 7061, Hydride AA EPA 206.2 or EPA 7060, Furnace AA
Barium (Ba)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 208.1 or EPA 7090, Flame AA EPA 208.2, Furnace AA
Beryllium (Be)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 210.1 or EPA 7090, Flame AA EPA 210.2A or EPA 7091, Furnace AA
Boron (B)	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic only	Cool, 4° C	6 months	Curcumin Colorimetric EPA 212.3

**** Each metal can also be analyzed by EPA 200.7, EPA 6010A, or EPA 6020.**

D. **METALS ANALYSIS (EPA Methods for Chemical Analysis of Water and Wastes, March 1983, or APHA Standard Methods, 15 Edition. and EPA SW-846, 3rd Edition) (continued)**

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Cadmium (Cd)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 213.1 or EPA 7130, Flame AA EPA 213.2 for EPA 7131, Furnace AA
Calcium (Ca)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 215.1 or EPA 7140, Flame AA
Chromium (Cr)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 218.1 or EPA 7190, Flame AA EPA 218.2 or EPA 7191, Furnace AA EPA 218.3 or EPA 7198, Chelation Extraction
Cobalt (Co)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 219.1 or EPA 7200, Flame AA EPA 219.2 or EPA 7201, Furnace AA
Copper (Cu)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 220.1 of EPA 7210, Flame AA EPA 220.2, Furnace AA
Gold (Au)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 231.1, Flame AA EPA 231.2, Furnace AA
Iron (Fe)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 236.1 or EPA 7380, Flame AA EPA 236.2, Furnace AA

**** Each metal can also be analyzed by EPA 200.7, EPA 6010A, or EPA 6020.**

D. **METALS ANALYSIS (EPA Methods for Chemical Analysis of Water and Wastes, March 1983, or APHA Standard Methods, 15 Edition. and EPA SW-846, 3rd Edition) (continued)**

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Lead (Pb)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 239.1 or EPA 7420, Flame AA EPA 239.2 or EPA 7421, Furnace AA
Magnesium (Mg)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 242.1 or EPA 7460, Flame AA
Manganese (Mn)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 243.1 or EPA 7480, Flame AA EPA 243.2 or EPA 7481, Furnace AA
Molybdenum (Mo)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 246.1 or EPA 7520, Flame AA EPA 246.2, Furnace AA
Nickel (Ni)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 249.1 or EPA 7610, Flame AA EPA 249.2, Furnace AA
Potassium (K)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 258.1, Flame AA
Selenium (Se)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 270.2 or EPA 7740, Furnace AA EPA 270.3 or EPA 7741, Hydride AA

**** Each metal can also be analyzed by EPA 200.7, EPA 6010A, or EPA 6020.**

D. **METALS ANALYSIS (EPA Methods for Chemical Analysis of Water and Wastes, March 1983, or APHA Standard Methods, 15 Edition. and EPA SW-846, 3rd Edition) (continued)**

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Silver (Ag)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 272.1 or EPA 7760, Flame AA EPA 272.2, Furnace AA
Sodium (Na)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 273.1 or EPA 7770, Flame AA
Thallium (Tl)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 279.1 or EPA 7840, Flame AA EPA 279.2 of EPA 7841, Furnace AA
Tin (Sn)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 282.1 or EPA 7870, Flame AA EPA 282.2, Furnace AA
Titanium (Ti)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 283.1, Flame AA EPA 283.2, Furnace AA
Vanadium (V)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 286.1 or EPA 7910, Flame AA EPA 286.2 or EPA 7911, Furnace AA
Zinc (Zn)**	100 ml for liquid sample Approximately 5 grams for solid samples	Plastic or Glass	HNO_3 to pH <2 Cool, 4° C	6 months	EPA 289.1 or EPA 7950, Flame AA EPA 289.2, Furnace AA

**** Each metal can also be analyzed by EPA 200.7, EPA 6010A, or EPA 6020.**

E. GENERAL: MINERAL ANALYSIS/VOLATILES - DRINKING WATER or TITLE 22 CAL/DOHS

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Complete General Mineral Analysis	1 - 2 liters	Plastic or Glass	Cool, 4° C, additional preservation depends on the analyte list	-----	-----
pH	50 ml	Plastic or Glass	None	Immediate	EPA Method 150.1 pH Meter
Alkalinity	50 - 100 ml	Plastic or Glass	Cool, 4° C	14 days	EPA Method 310.1 Titrimetric Method
Calcium**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	Flame AA EPA 215.1
Chloride	50 - 100 ml	Plastic or Glass	Cool, 4° C	28 days	EPA Method 325.3 Titrimetric Method
Copper**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	Flame AA EPA 220.1
MBAS	500 ml	Plastic or Glass	Cool, 4° C	48 hours	EPA Method 425.1 Colorimetric
Iron**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	Flame AA EPA 236.1
Magnesium**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	Flame AA EPA 242.1
Manganese**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	Flame AA EPA 243.1
Sodium**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	Flame AA EPA 273.1
Sulfate	50 - 100 ml	Plastic or Glass	Cool, 4° C	28 days	EPA 375.4 Turbidimetric
Electrical Conductivity	50 - 100 ml	Plastic or Glass	Cool, 4° C	24 hrs. or filter	EPA Method 120.1 EC Water
Total Dissolved Solids	100 ml	Plastic or Glass	Cool, 4° C	7 days	EPA Method 160.1 Gravimetric
Total Hardness	50 - 100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	EPA Method 130.2 Titrimetric Standard Method 314-A Calculation
Zinc**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	Flame AA EPA 289.1
Volatile Organics (VOAs)	2 - 40 ml containers	Glass, Cap teflon-lined, 40 ml.	No headspace, HCl to pH<2, if residual chlorine then preserve with Na_2SO_4 or Ascorbic Acid Wash. State - No headspace and HCl to pH <2 only	14 days	EPA Method 524.2

**** Each metal can also be analyzed by EPA 200.7 or EPA 6010A.**

F. INORGRANIC ANALYSIS: DRINKING WATER or TITLE 22 - CAL/DOHS

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Arsenic**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	EPA 206.3, Furnace AA
Barium**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	EPA 208.1, Flame AA
Cadmium**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	EPA 213.1 , Flame AA or EPA 218.2, Furnace AA
Chromium**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	EPA 218.1, Flame AA EPA 218.2, Furnace AA
Lead**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	EPA 239.2, Furnace AA
Mercury	100 ml	Plastic or Glass	HNO_3 to pH <2	28 days	EPA 245.1 ,Cold Vapor
Selenium**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	EPA 270.2 ,Furnace AA
Silver**	100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	EPA 272.1 ,Flame AA
Nitrate-Nitrogen	50 ml	Plastic or Glass	Cool, 4° C add H_2SO_4 to pH <2	14 days	EPA 352.1, Brucine Sulfate
			Cool, 4° C	48 hours	EPA 353.3, Cadmium Reduction
Fluoride	300 ml	Plastic or Glass	None	28 days	EPA 340.2, Ion Selective Electrode

**** Each metal can also be analyzed by EPA 200.7 or EPA 200.8.**

G. GENERAL PHYSICAL ANALYSIS: DRINKING WATER or TITLE 22 - CAL/DOHS

PARAMETER	VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Color	50 ml	Plastic or Glass	Cool, 4° C	48 hours	EPA Method 110.2
Odor	200 ml	Plastic or Glass	Cool, 4° C	48 hours	EPA Method 180.1, Threshold Odor
Turbidity	100 ml	Plastic or Glass	Cool, 4° C	48 hours	EPA Method 180.1, Nephelometric

H. GENERAL WET CHEMISTRY AND MISCELLANEOUS ANALYSIS

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Acidity	100 ml	Plastic or Glass	Cool, 4° C	14 days	EPA 305.1, Titrimetric
Alkalinity	50-100 ml	Plastic or Glass	Cool, 4° C	14 days	EPA 310.1 ,Titrimetric
Ammonia Nitrogen	100 ml	Plastic or Glass	Cool, 4° C H_2SO_4 to pH <2	28 days	EPA 350.1, Colorimetric
BOD	1 liter	Plastic or Glass	Cool, 4° C	48 hours	EPA 405.1
Boron	100 ml	Plastic	None	28 days	EPA 212.3 ,Curcumin
Chloride	100 ml	Plastic or Glass	None	28 days	EPA Method 325.3, Mercuric Nitrate or EPA 300.0, Ion Chromatography
COD	20 ml	Plastic or Glass	Cool, 4° C H_2SO_4 to pH <2	28 days	EPA Methods 410.4, Colorimetric
Coliform Fecal Coliform	100 ml	Sterilized Plastic Bottles	Cool, 4° C $Na_2S_2O_3$ preserved for presence of free chlorine	6 hours or 30 hours depending on the test requested	Standard Method 909A or 909C
Color	50 ml	Plastic or Glass	Cool, 4° C	48 hours	EPA 110.2 or 110.3
Cyanide	500 ml	Plastic or Glass	Cool, 4° C NaOH to pH >12	14 days	EPA 335.3, Colorimetric
Electrical Conductivity	50 - 100 ml	Plastic or Glass	Cool, 4° C	28 days	EPA 120.1, EC Meter
Fluorides	300 ml	Plastic or Glass	None	28 days	EPA 340.2, Ion Specific Electrode or EPA 300.0, Ion Chromatography
MBAS	500 ml	Plastic or Glass	Cool, 4° C	48 hours	EPA 425.1, Colorimetric

H. GENERAL WET CHEMISTRY AND MISCELLANEOUS ANALYSIS (continued)

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Nitrate Nitrogen	100 ml	Plastic or Glass	Cool, 4° C	14 days	EPA 300.0, Ion Chromatography
Nitrate Nitrite Nitrogen	100 ml	Plastic or Glass	Cool, 4° C Add H_2SO_4 to pH <2	14 days	EPA 353.3, Cadmium Reduction
Nitrite Nitrogen	50 ml	Plastic or Glass	Cool, 4° C	48 hours	EPA 354.1, SPectrophotometric
Odor	200 ml	Plastic or Glass	Cool, 4° C	24 hours	EPA 140.1
Oil and Grease	1 liter	Glass	Cool, 4° C Add H_2SO_4 to pH <2	28 days	EPA 413.1, Gravimetric
Orthophosphate	50 ml	Plastic or Glass	Cool, 4° C	48 hours	EPA 365.2, Ascorbic Acid
pH	50 ml	Plastic or Glass	None	Immediate	EPA Method 150.1, pH Meter
Phenolics	500 ml	Glass	Cool, 4° C Add H_2SO_4 to pH <2	28 days	EPA 420.1, 4-AAP
Radioactivity	1-18 liters	Plastic or Glass Glass only for Tritium	HCl or HNO_3 * to pH <2 *Some exceptions	-----	Standard Method 701
Silica	50 ml	Plastic	Cool, 4° C	28 days	EPA 370.1, Colorimetric Flame AA Method
Sulfates	50 ml - 100 ml	Plastic or Glass	Cool, 4° C	28 days	EPA 375.4, Turbidimetric or EPA 300.0, Ion Chromatography
Sulfides	500 ml	Plastic or Glass	NaOH to pH >9 2 ml Zinc Acetate Cool, 4° C	7 days	EPA 376.1 ,Titrimetric
Sulfites	50 ml	Plastic or Glass	None	Immediate	EPA 377.1 ,Titrimetric
TOC	25 ml	Plastic or Glass	Cool, 4° C H_2SO_4 to pH <2	28 days	EPA 415.2, TOC Analyzer
Total Dissolved Solids	100 ml	Plastic or Glass	Cool, 4° C	7 days	EPA 160.1, Gravimetric

H. GENERAL WET CHEMISTRY AND MISCELLANEOUS ANALYSIS (continued)

PARAMETER	MINIMUM VOLUME REQUIRED	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	METHOD FOR ANALYSIS
Total Hardness	50-100 ml	Plastic or Glass	HNO_3 to pH <2	6 months	EPA 130.2, Titrimetric Standard Method 314-A Calculation
Total Kjeldahl Nitrogen	1 liter	Plastic or Glass	Cool, 4° C Add H_2SO_4 to pH <2	28 days	EPA 351.4, Ion Specific Electrode
Total Organic Nitrogen TON-TKN-NH_3-N	1 liter	Plastic or Glass	Cool, 4° C Add H_2SO_4 to pH <2	28 days	EPA 351.4 and EPA 350.3
Total Petroleum Hydrocarbons Scan, by GC	400 ml to 1 liter Approximately 50 grams for a solid sample	Glass	Cool, 4^0 C	14 days, but this may vary between states so regulations must be consulted	WTPH-HCID by GC/FID or Modified Method 8015, GC
Total Petroleum Hydrocarbons as Gas, by GC	40 ml Approximately 20 grams for a solid sample	Glass	Cool, 4^0 C, Methanol preservation may be a requirement of some states so state regulations must be consulted Cool, 4^0 C	14 days	WTPH-G by purge and trap GC/FID or Modified Method 8015, GC/FID
Total Petroleum Hydrocarbons as Diesel, by GC	1 liter Approximately 50 grams for a solid sample	Glass	Cool, 4^0 C	14 days	WTPH-D by GC/FID or Modified Method 8015, GC/FID
Total Phosphate	50 ml	Plastic or Glass	Cool, 4° C Add H_2SO_4 to pH <2	28 days	EPA 365.4, Colorimetric
Total Residue	100 ml	Plastic or Glass	Cool, 4° C	7 days	EPA 160.3 , Gravimetric
Total Settleable Solids	1 liter	Plastic or Glass	Cool, 4° C	48 hours	EPA 160.5, Imhoff Cone
Total Suspended Solids	100 ml	Plastic or Glass	Cool, 4° C	7 days	EPA 160.2, Gravimetric
Total Volatile Solids	100 ml	Plastic or Glass	Cool, 4° C Add H_2SO_4 to pH <2	7 days	EPA 160.4, Gravimetric
TOX	500 ml	Amber Glass, Teflon Septum	Cool, 4° C Add H_2SO_4 to pH <2	7 days	EPA 450.1 or EPA 9020, TOX Analyzer
Turbidity	100 ml	Plastic or Glass	Cool, 4° C	48 hours	EPA 180.1

APPENDIX 8

Checklist For Analyses With Short Holding Times

CHECKLIST FOR ANALYSES WITH SHORT HOLDING TIMES

To be completed prior to release of release of samples to laboratory

_____ Correct test codes are entered

_____ Dates and times received and collected are correct

_____ Matrices are correct

_____ Sample I.D.s are correct

I certify that all of the above have been checked and were found accurately entered in the LIMS.

_____ _____
(Signature) (Date)

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-6006

Title: Cation-Exchange Capacity of Soils (Sodium Acetate) by SW 846 Method 9081

Revision history:

Number	Date
0	1/25/99

UNCONTROLLED

Written by: Harry Romberg Date: 1-25-99
Harry Romberg, Quality Assurance Officer

Reviewed by: Raul N Date: 1/25/99
Raul Nino, Analyst

Approved by: Kathy Kreps Date: 1/25/99
Kathy Kreps, Laboratory Director

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1. Introduction and Scope

1.1 Scope

1.1.1 LTL-6006 (SW 846 Method 9081) is applicable to most soils, including calcareous and noncalcareous soils. This method only applies to the Cation Exchange Capacity extraction. The actual analysis method should be referred to for quantitation of sodium in the extract.

1.2 Method Description

1.2.1 The soil sample is mixed with an excess of sodium acetate solution, resulting in an exchange of the added sodium cations for the matrix cations. Subsequently, the sample is washed with isopropyl alcohol. An ammonium acetate solution is then added, which replaces the adsorbed sodium with ammonium. The concentration of displaced sodium is then determined by flame atomic absorption spectroscopy or ICP.

1.2.2 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.3 Sample Collection, Sample Storage, Holding Times

1.3.1 No holding times or preservation are specified for this method.

1.4 Definition of Terms

1.4.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

1.4.2 Batch Identifier - A number given to each preparation or analysis group which uniquely identifies that batch. This number is generally the blank ID for preparation batches and either a sequence number for organic analyses or an analysis number which is similar to the blank ID, only preceded by an "A" rather than a "B" for inorganic batches. This is followed by the date, analysis, matrix and sequence number (i.e. BmmddyyCECS01).

1.4.3 CLP - Contract Laboratory Program - The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.

1.4.4 DIW - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

1.4.5 RPD - Relative percent difference, in this case between duplicate analyses, calculated as the difference between replicate sample determinations divided by the average calculated as a percent.

2. Equipment List and Standards

2.1 Equipment

- 50 mL centrifuge tubes and stoppers
- mechanical shaker
- 100 mL class A volumetric flasks

2.2 Reagents

2.2.1 Sodium acetate (NaOAc), 1.0 N: Dissolve 136 g of $NaC_2H_2O_2 \cdot 3H_2O$ (or 82 g anhydrous $NaC_2H_2O_2$) in water and dilute it to 1,000 mL. The pH of this solution should be 8.2. If needed, add a few drops of acetic acid or NaOH solution to bring the reaction of the solution to pH 8.2.

2.2.2 Ammonium acetate (NH_4OAc), 1 N: Dilute 114 mL of glacial acetic acid (99.5%) with water to a volume of approximately 1 liter. Then add 138 mL of concentrated ammonium hydroxide (NH_4OH) and add water to obtain a volume of about 1,980 mL. Check the pH of the resulting solution, add more NH_4OH, as needed, to obtain a pH of 7, and dilute the solution to a volume of 2 liters with water.

2.2.3 Isopropyl alcohol: 99%.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.4 Electrical shock - All instruments present the possibility of electrical shock The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.2 Waste Disposal

3.2.1 Isopropyl alcohol solutions should be disposed of in the solvent waste container.

3.2.2 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

4. Calibration and Quality Control

4.1 Method Blanks

4.1.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time or at least one blank every 20 samples which ever is more frequent. Any analyte response above the reporting limit is reported. Method blank control limits are that contamination should not exceed the reporting limit.

4.1.2 Corrective action

4.1.2.1 Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if an analyte were found in the blank but not in any of the associated samples then sample group may not require re-analysis. In addition, if sample levels exceed 20 times the blank, the level of contamination may be considered insignificant. In any case, if re-preparation and re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Control Officer. It is the laboratory's responsibility to ensure that method interferences caused by contaminants in acids, solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the analytical run be minimized. In the extreme case of chronic contamination, blanks may have to be analyzed from each stage of the sample processing to determine the contamination source so it can be eliminated. In all cases where blank contamination exceeds the control limit, a narrative comment must be made which documents the corrective actions taken.

4.2 Sample Duplicate

4.2.1 Criteria

4.2.1.1 At least one duplicate sample per 10 samples is required. RPD values are calculated in a manner similar to MS/MSD RPDs:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where:
S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analysis

4.2.1.2 The RPD control limits are detailed in the Quality Control Database (QC_DB) and will change from time to time.

4.2.2 Corrective action

4.2.2.1 If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation procedures

5.1 Extraction Procedure

5.1.1 Weigh 4 g of medium or fine-textured soil or 6 g of coarse-textured soil and transfer the sample to a 50-mL, round-bottom, narrow-neck centrifuge tube. (A fine soil has >50% of the particles <0.074 mm, medium soil has >50% >0.425 mm, while a coarse soil has more than 50% of its particles >2 mm.

5.1.2 Add 33 mL of 1.0 N NaOAc solution, stopper the tube, shake it in a mechanical shaker for 5 min, and centrifuge it until the supernatant liquid is clear.

5.1.3 Decant the liquid, and repeat Paragraph 5.1.2 three more times.

5.1.4 Add 33 mL of 99% isopropyl alcohol, stopper the tube, shake it in a mechanical shaker for 5 min, and centrifuge it until the supernatant liquid is clear.

5.1.5 Repeat the procedure described in Paragraph 5.1.4 two more times.

5.1.6 Add 33 mL of NH_4OAc solution, stopper the tube, shake it in a mechanical shaker for 5 min, and centrifuge it until the supernatant liquid is clear. Decant the washing into a 100-mL volumetric flask.

5.1.7 Repeat the procedure described in Paragraph 5.1.6 two more times.

5.1.8 Dilute the combined washing to the 100-mL mark with ammonium acetate solution and determine the sodium concentration by atomic absorption, emission spectroscopy, or an equivalent method.

5.2 Instrumental Analysis

5.2.1 Specifics of the instrumental analysis are contained in the appropriate SOP.

6. Reports

6.1 Data Packet Organization

6.1.1 Sample reports vary depending upon the needs of the client. They may be as simple as a standard laboratory report with only a QC summary (generated from QC_DB) or they may be more thorough and include instrument calibration information and raw data if a full data package is required.

6.2 Quality Control Reports

6.2.1 All results for quality control tests are entered into the lab data base using the QC_DB program. Printouts of all data entered must be included in the data packet. The routine minimum for this analysis is a method blank report and a duplicate report.

6.3 Sample Result Reports

6.3.1 Data Qualifying Flags

6.3.1.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

CODE	Definition
U	: The analyte of interest was not detected, to the limit of detection indicated.

Appendix I

QC Summary Table

Laucks Testing Laboratories

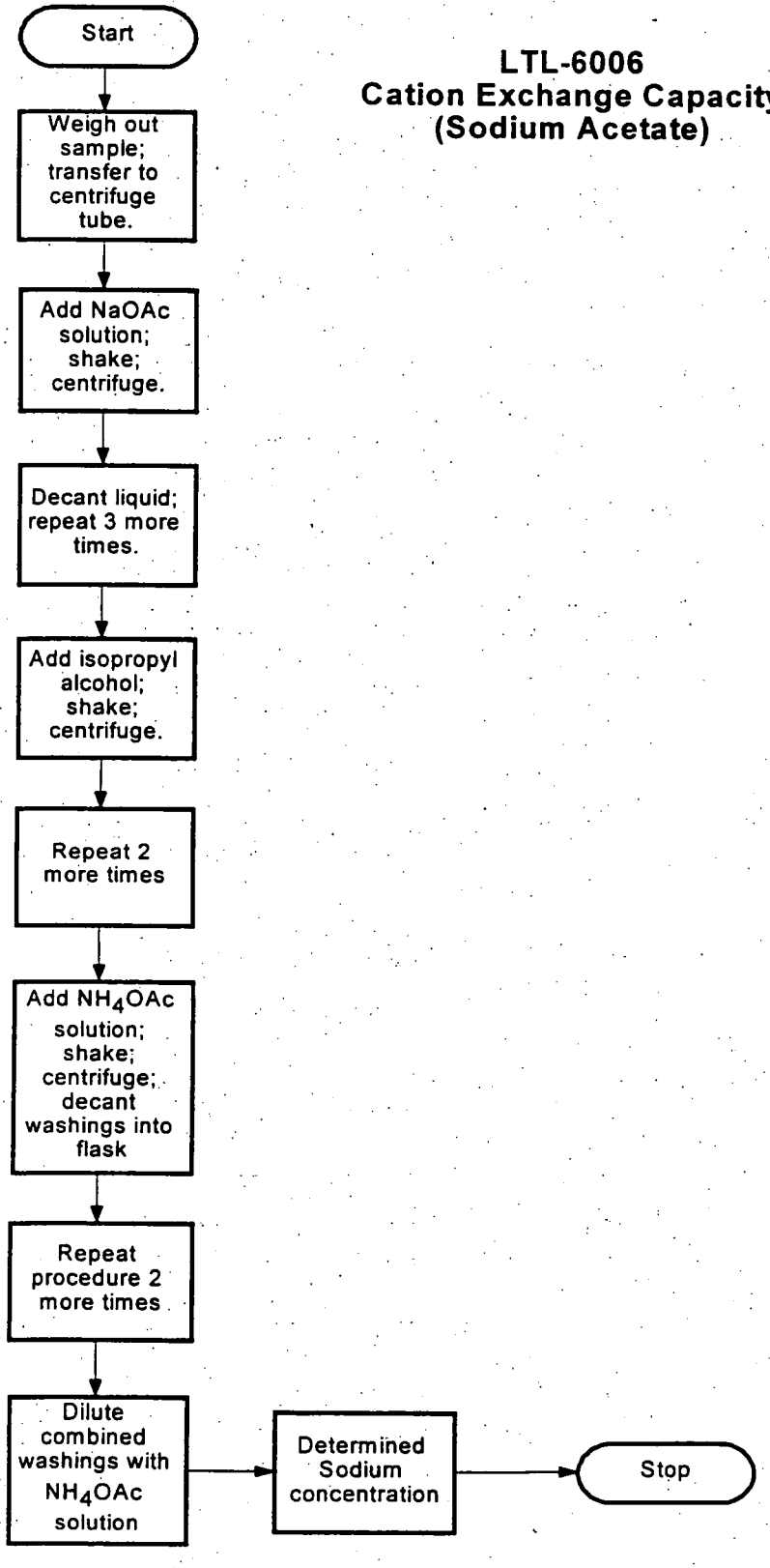
Method LTL-6006 QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Method Blank	None	No blank above reporting limit	1 per 20 samples or one per batch	reanalyze unless samples >20X blank	QC_DB and sample report
Duplicate % Difference or RPD	None	See QC_DB database	1 per 10 samples or one per batch	Discuss with QC Officer	QC_DB and sample report

Appendix II

Flow Chart

LTL-6006
Cation Exchange Capacity
(Sodium Acetate)



LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-7003

Title: **Inorganic Glass Cleaning Procedure**

Revision history:

Number	Date
2	04/09/97
1	01/05/88

Written by: Bill Lundberg Date: 4/9/97
Bill Lundberg, Inorganics Supervisor

Reviewed by: Harry Romberg Date: 4-9-97
Harry Romberg, QA Officer

Approved by: Karen J. Kotz Date: 4/9/97
Karen Kotz, Laboratory Director

UNCONTROLLED

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1. Introduction and Scope

1.1 Method Description

1.1.1 The purpose of this SOP is to define the procedures used in the inorganics department for the cleaning of glassware. The objective is to define a specific method of cleaning that is adapted to both the substances that are to be removed, and the determination to be performed.

1.2 Definitions

1.2.1 DIW = deionized water

2. Equipment List and Standards

2.1 Standard laboratory glassware, including but not limited to:

2.1.1 Volumetric flasks
Beakers
Funnels
Separatory funnels
Kjeldahl flasks
Nessler tubes
Erlenmeyer flasks
Burets
BOD bottles
Distillation Apparatus

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 Several cleaning procedures or soaking procedures require the use of a chromic acid cleaning solution, concentrated HNO_3 or H_2SO_4. USE APPROPRIATE SAFETY PRECAUTIONS FOR ACID USE! Wear safety glasses, lab coat, and gloves.

3.1.2 Some oily samples or profile samples may require the use of acetone or chloroform to clean the glassware. AGAIN, USE APPROPRIATE SAFETY PRECAUTIONS FOR SOLVENT USE! Wear safety glasses, lab coat, and gloves. Dispose of solvent waste in appropriate solvent waste barrel.

3.1.3 Some profile-type samples may not clean up even with solvent washes, and therefore may need to be baked in the muffle furnace at 500 degrees C for 1-3 hours.

3.1.4 CAUTION: Be sure to evaporate any residual solvent from glassware before putting in muffle furnace.

3.1.5 Do not put soft glass (non-pyrex, kimax, etc.) in a muffle furnace or it will shatter. Take appropriate precautions with hot materials.

4. Operation procedures

4.1.1 All glassware must be scrupulously cleaned. The analyst that performs each specific analysis is responsible for the proper cleaning of his or her own glassware. Glassware used in routine analysis is kept separate from the general use glassware. Specific cleaning procedures are listed by type of analysis.

4.1.2 ALKALINITY

4.1.2.1 Glassware Erlenmeyer flasks

4.1.2.2 Buret

4.1.2.3 Cleaning Procedures - Rinse with DIW.

4.1.2.4 Air dry.

4.1.3 AUTO ANALYZER (refer to the applicable analytical SOP)

4.1.4 BOD

4.1.4.1 Glassware BOD bottles

4.1.4.2 Glass pipettes

4.1.4.3 Cleaning procedure - Wash with hot tap water and Alconox.

4.1.4.4 Rinse with hot tap water.

4.1.4.5 Rinse with DIW.

4.1.4.6 Air dry.

4.1.5 COD

4.1.5.1 Procedure for Glassware Condensers, Erlenmeyer flasks, Buret

4.1.5.2 Cleaning Procedure - Rinse well with DIW only.

4.1.5.3 Soaking Procedure - Acid soak flasks with C.O.D. acid for 10 minutes prior to use. Rinse well with DIW.

4.1.6 CYANIDE

4.1.6.1 Procedure for Glassware, Volumetric flasks, Distillation apparatus

4.1.6.2 Cleaning procedure for Flasks - DIW rinse only.

4.1.6.3 Distillation apparatus - occasional H_2SO_4 and DIW wash, but generally DIW rinsed only.

4.1.7 Hexavalent Chromium

4.1.7.1 Cleaning procedure - Wash with hot tap water and Alconox.

4.1.7.2 Rinse well with DIW.

4.1.7.3 Air dry.

4.1.8 FORMALDEHYDES

4.1.8.1 Procedure for GlasswareBeakers, Erlenmeyer flasks, Volumetric flasks, Test tubes

4.1.8.2 Cleaning procedures - ,Rinse well with DIW only.

4.1.8.3 Never contaminate glassware with HNO_3 .

4.1.9 HARDNESS

4.1.9.1 Procedure for Glassware, Erlenmeyer flasks, Buret

4.1.9.2 Cleaning procedure - Rinse with DIW only.

4.1.10 KJELDAHL NITROGEN-LOW LEVELS (TKN AND AMMONIA)

4.1.10.1 Procedure for Glassware, Kjeldahl distillation apparatus, Kjeldahl flasks, Erlenmeyer, flasks or beakers

4.1.10.2 Cleaning procedure for Kjeldahl flasks - pre-distill with DIW and NaOH, and do final DIW rinses.

4.1.10.3 Beakers or Erlenmeyer flasks- DIW rinse only.

4.1.11 OIL AND GREASE

4.1.11.1 Procedure for Glassware, Volumetric flasks, Beakers, Funnels, Separatory funnels, Soxhlet digestion apparatus

4.1.11.2 Cleaning procedure for Vol. flasks, funnels, soxhlet apparatus- freon rinse 3-4 times.

4.1.11.3 Cleaning procedure for Beakers, separatory funnels- hot tap water and Alconox, rinse well with hot tap water, and dry.

4.1.12 METALS (INCLUDING HYDRIDES AND MERCURY)

4.1.12.1 Procedure for Glassware, Volumetric flasks, Beakers, Erlenmeyer flasks, BOD bottles, Digestion caps or watchglasses

4.1.12.2 Cleaning procedure - Rinse well with DIW only.

4.1.12.3 OPTIONAL:

4.1.12.4 If oily or difficult to clean, wash with acetone, scrub with hot tap water and Alconox, and rinse well with DIW.

4.1.12.5 Concentrated acid wash and DIW rinsed.

4.1.12.6 Bake in muffle furnace at 550 degrees C for 1 hour and rinse well with DIW.

4.1.12.7 NOTE: Some metals glassware should not be cleaned with Alconox at all.

4.1.12.8 Soaking procedure - Acid soak all metals glassware in HNO_3 and DIW.

4.1.12.9 Fill glassware with DIW and add 4-8 mls HNO_3. Cover and store until next use.

4.1.13 PHENOL

4.1.13.1 Procedure for Glassware, Kjeldahl flasks, Erlenmeyer flasks

4.1.13.2 Cleaning procedure for Kjeldahl flasks - pre-distill with H_2SO_4 and catalyst, DIW rinse.

4.1.13.3 Cleaning procedure for Erlenmeyer flasks - acid H_2SO_4 wash and DIW rinse.

4.1.13.4 NOTE: Use only those Kjeldahl flasks designated for use in phenol distillations.

4.1.14 PHOSPHATE

4.1.14.1 Cleaning procedure for GlasswareBeakers

4.1.14.2 Acid wash with H_2SO_4 .

4.1.14.3 Rinse with DIW.

4.1.15 TOC (SOILS)

4.1.15.1 Glassware, TOC combustion boats

4.1.15.2 Cleaning procedure - Brush out last sample.

4.1.15.3 Incinerate boat in muffle furnace at 950 degrees C.

4.1.16 TOX

4.1.16.1 Cleaning procedure for Glassware, Volumetric flasks, Misc. TOX glass parts

4.1.16.2 Cleaning procedure - Soak in chromic acid solution.

4.1.16.3 Wash with hot tap water and alconox.

4.1.16.4 Rinse well with DIW.

4.1.16.5 Bake in muffle furnace at 400 degrees C.

4.1.16.6 Cool.

4.1.16.7 Store in glass teflon sealed container inside a dessicator.

5. References

5.1.1 See the applicable analytical or preparation SOP for specific cleaning issues and references.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-7009

Title: **Microwave Assisted Acid Digestion of Aqueous Samples and Extracts Using SW846 Method 3015**

Revision history:

Number	Date
1.	04/20/95
2.	06/04/96

UNCONTROLLED

Written by: Lucas Hawkins — Date: 6/4/96
Lucas Hawkins, Chemist

Reviewed by: Mark J. Strongman — Date: 6.4.96
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Reviewed by: Bill Lundberg — Date: 6/4/96
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Reviewed by: Harry Romberg — Date: 6-4-96
Harry Romberg, QC Officer

Approved by: Karen J. Kotz — Date: 6/4/96
Karen Kotz, Laboratory Director

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1. Introduction and Scope

1.1 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis by flame atomic absorption spectroscopy (FLAA), graphite furnace absorption spectroscopy (GFAA), inductively coupled argon plasma spectroscopy (ICP), or inductively coupled argon plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determination of available metals.

1.3 Samples prepared by Method 3015 using nitric acid digestion may be analyzed by FLAA, GFAA, ICP or ICP-MS for the following:

Aluminum	Calcium	Lead	*Selenium
Antimony	Chromium	Magnesium	Silver
*Arsenic	Cobalt	Manganese	Sodium
Barium	Copper	Molybdenum	Thallium
Beryllium	Iron	Nickel	Vanadium
Cadmium	Zinc	Potassium	

*Cannot be analyzed by FLAA

1.4 Microwave power settings and times used in this SOP are based on manufacturers recommendation. Laucks system is different from the design used in both the SW846 and EPA CLP publications, in that it uses a 12 place carousel rather than 5 and that our system does not currently allow us to monitor the temperature in the vessels.

2. Summary of Method

2.1 Nitric acid is added to an aqueous sample in a 120 mL Teflon® digestion vessel. The vessel is capped and heated in a microwave unit. After cooling, the vessel contents are filtered, or allowed to settle in a clean sample bottle for analysis.

3. Safety Procedures

3.1 These procedures involve the use of strong and/or hot acid solutions. The analyst must wear eye protection, a lab coat, and gloves to protect against burns.

3.2 Samples and spiking solutions may contain high levels of toxic metals and other unknown constituents. The analyst must take every precaution to avoid contact with these

potentially hazardous materials and should wash hands thoroughly before eating or leaving the laboratory.

3.3 Very reactive or volatile materials may create high pressures when heated, causing the vessels to vent with potential loss of sample and analytes. Samples that contain carbonates or other carbon dioxide generating compounds may generate enough pressure to vent the vessel. If this situation is anticipated the analyst may wish to use a smaller sample or an alternative digestion method.

4. Equipment

- MDS-205 Microwave Digestion system, CEM
- Capping station
- Carousel
- 120 mL Teflon® vessels and caps
- 50 or 100 mL graduated cylinder, acid washed
- Glass funnels, acid-washed
- Filter paper, Whatman No. 41 or equivalent
- Sample digestate bottles, acid washed
- Analytical balance, 300 g capacity, minimum ± 0.01 g.

Note: All glassware used for this digestion must be prepared by the method stated in Inorganics Glassware Cleaning Procedures, LTL-7003.

4.1 All Teflon® vessels and caps are to be thoroughly rinsed with deionized water prior to digestions and shaken to remove any significant droplets in the vessels.

4.2 The microwave is to be calibrated by using the method stated in SW846 method 3051.

5. Reagents

5.1 Reagent Water - Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified.

5.2 Nitric acid (concentrated), HNO_3, ACS Reagent grade or better

The method blank, prepared along with the samples, is used as a contamination check. Since the holding time for all analytes associated with this method have a holding time of 6 months, repreparation would not be an issue if contamination was traced to a specific reagent.

6. Microwave Sample Digestion Procedure

See Appendix A for sample digestion log.
See Appendix B for flowchart.
See Appendix C for QC Solutions

6.1 A 45 mL aliquot of well shaken sample is measured into a graduated cylinder. This aliquot is poured into the Teflon® digestion vessel with the number of the vessel recorded on the preparation sheet.

6.2 A blank sample of reagent water is treated in the same manner along with spikes , duplicates, and laboratory control samples. If only one graduated cylinder is used for all samples, the preparation blank is to be the last sample dispensed to assure the absence of sample carry-over.

6.3 Add 5 mL of concentrated nitric acid to each vessel and cap hand tight. For each microwave digestion run, a double ported lid is to accompany the sample that seems to have the most carbon. Weigh each capped vessel to the nearest 0.01 g.

6.4 Place the carousel in the unit and attach the pressure control line to the digestion vessel with the double ported lid. Set the first program to run at 100% power for approximately 15 minutes., and the second program for 100% power for 10 minutes. Adjust the pressure control unit to 70 psi. After starting the microwave, monitor the pressure until it reaches the 70 psi limit. Advance the microwave to the second program and re-start.

6.5 At the end of the microwave program, allow the vessels to cool for at least 5 minutes in the unit before removal to avoid possible injury if a vessel vents immediately after microwave heating. Cool the samples before re-weighing to determine the extent of sample loss if any. If the weight of the sample plus acid has decreased by more than 10%, discard and prepare the sample again.

6.6 Uncap the vessels and transfer the samples to an acid-cleaned polyethylene bottle. If the digested sample contains particulate which may clog nebulizers or interfere with injection of the sample into an instrument, the sample may be allowed to settle or be filtered.

6.7 The prepared samples are then transferred to the metals analysis department. The digestion log is to reflect the time at the start and finish of the digest. In order to maintain a strict chain of custody, the time and date when the digestates are relinquished to the analysis department, as well as the initials of the analyst accepting the digestates, are recorded on the digest log

7. Quality Control

7.1 In each batch or SDG consisting of no more than 20 samples, a preparation blank is created. The blank should be labeled on the digestate bottle in the following way: B, date,

M (microwave), W (water) and the sequence number of the digestion. Example B022095MW01.

7.2 Spiked samples should be employed to determine accuracy. In each batch or SDG consisting of no more than 20 samples, either matrix spike / sample duplicate (MS/Dup) or matrix spike /matrix spike duplicate (MS/MSD) samples will be prepared. For SW3015-specified quality control measures, MS/Dup samples will be prepared in the following way. Dispense a sample in triplicate. Two will be analyzed exactly as any other sample. The third must be spiked with the appropriate spike solutions, determined by the analyst. All glassware and digestate bottles must be marked appropriately. If MS/MSD samples are required instead of the SW846-specified MS/Dup, both the second and third aliquot must be spiked.

7.3 In each batch or SDG consisting of no more than 20 samples, prepare a Lab Control Sample (LCSW) in exactly the same manner as a sample. Each spiking solution is given its own unique number according to the page and line of the standards logbook which it is entered into. This number and the volume dispensed must be clearly recorded on the digestion log. A sample page from the standards logbook is included in Appendix C.

8. References

8.1 USEPA, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, USEPA SW846, most recent version, Method 3015.

Appendix A, Sample LTL-7009 Digestion Log

Laucks Testing Laboratories, INC.	START DATE TIME	FINISH DATE TIME	METHOD	ANALYST	ANALYSIS
SDG #:			SW846		Microwave
MATRIX: WATER			3015		Digestion

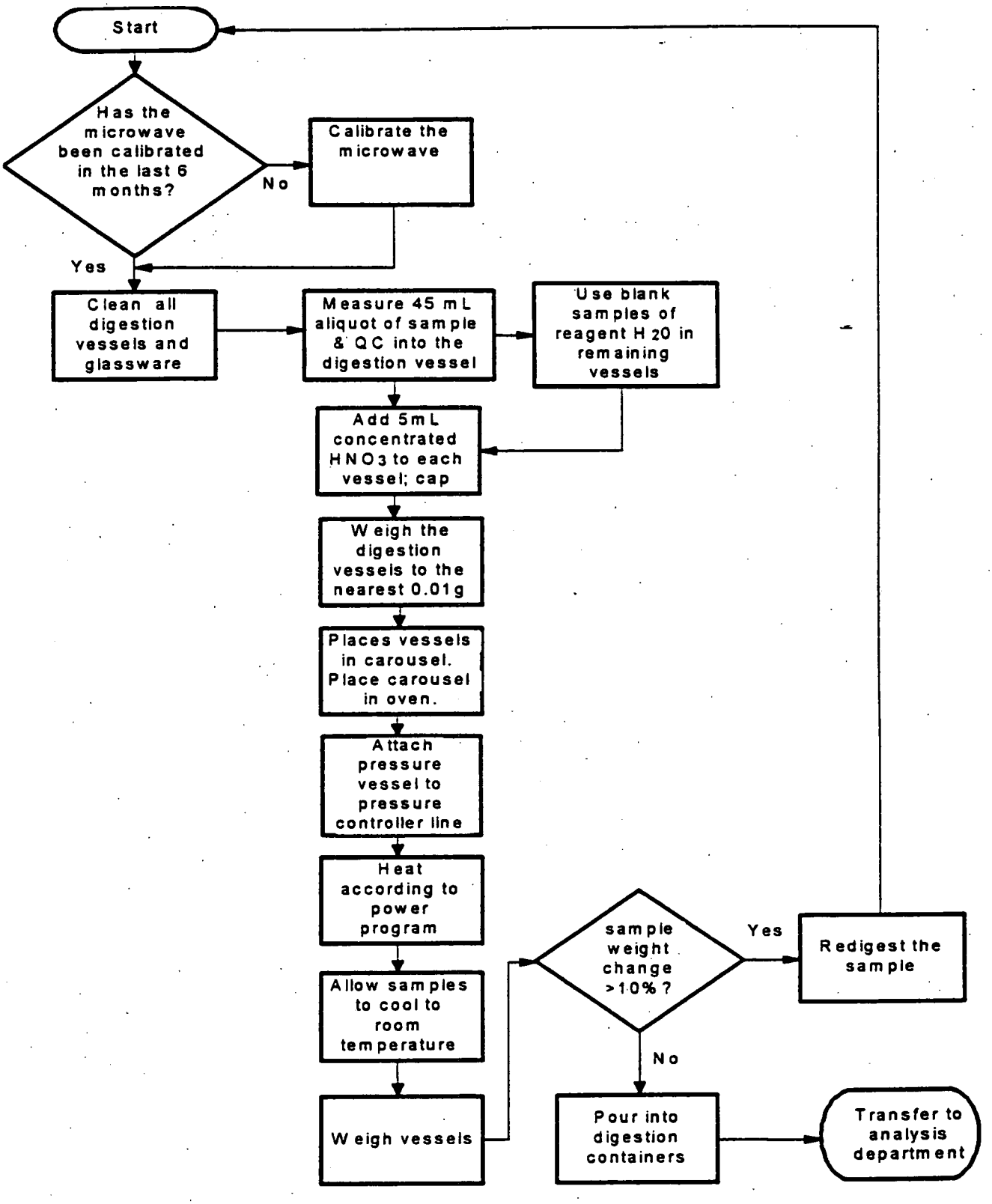
Bomb #	Sample ID	Samp Vol (mL)	Final Vol (mL)	Color		Clarity		Bomb & Sample (g)	Final Bomb (g)	Δ (g)	Δ >2.5 g ?
				Int	Fin	Int	Fin				

Chain of Custody	Digest Relinquished Date / Time : Analyst	Digest Accepted :Analyst	Digest Disposed :Date
	/ :		

COLOR: 1 = Red, 2 = Blue, 3 = Yellow, 4 = Green, 5 = Orange, 6 = Violet, 7 = White, 8 = Brown, 9 = Gray, 10 = Black, 11 = Colorless.

CLARITY: 1 = Clear, 2 = Cloudy, 3 = Opaque.

Appendix B, Flowchart for LTL-7009


Start
Has the microwave been calibrated in the last 6 months?
No
Calibrate the microwave
Yes
Clean all digestion vessels and glassware
Measure 45 mL aliquot of sample & QC into the digestion vessel
Use blank samples of reagent H 20 in remaining vessels
Add 5mL concentrated HNO3 to each vessel; cap
Weigh the digestion vessels to the nearest 0.01g
Places vessels in carousel. Place carousel in oven.
Attach pressure vessel to pressure controller line
Heat according to power program
Allow samples to cool to room temperature
Weigh vessels
sample weight change >10% ?
Yes
Redigest the sample
No
Pour into digestion containers
Transfer to analysis department

Appendix C, Quality Control Solutions

ICP LCSW

The LCSW for the ICP digest was made by diluting 100 mLs of SPEX ICV-1™ solution to 1000 mLs with type II water. A 100 mL aliquot of this solution was then digested.

ICP Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
Al	20000	Pb	500
Ba	20000	Mg	500000
Be	500	Mn	1500
Cd	500	Ni	4000
Ca	500000	K	500000
Cr	1000	Ag	1000
Co	5000	Na	500000
Cu	2500	V	5000
Fe	10000	Zn	2000
Sb	6000		

Other Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
As	1000	Tl	1000
Se	500		

Tables based on a final volume of 100 mL.

Graphite Furnace LCSW

The LCSW for the Graphite Furnace digest was made by diluting 100 mLs of SPEX ICV-1™ solution to 1000 mLs with Type II water. A 10 mL aliquot of this solution was added to 90 mL of Type II water and then digested.

Graphite Furnace Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
As	100	Tl	100
Pb	50	Sb	600
Se	50		

Other Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
Al	2000	Pb	50
Ba	2000	Mg	50000
Be	50	Mn	150
Cd	50	Ni	400
Ca	50000	K	50000
Cr	100	Ag	100
Co	500	Na	50000
Cu	250	V	500
Fe`	1000	Zn	200

Tables based on a final volume of 100 mL.

ICP Spikes

- The CLP spike solution for ICP digest was made by diluting 10 mLs of CLPP-SPK-1™, 10 mLs of CLPP-SPK-2™, and 10 mLs of CLPP-SPK-3™ to 100 mLs with Type II water.

- Add 1000 µLs of CLP spike solution to water samples and 2000 µLs of CLP spike solution to soil samples prior to digestion.

ICP Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
Ag	50	Fe	1000
Al	2000	Mn	500
As	2000	Ni	500
Ba	2000	Pb	500
Be	50	Se	2000
Cd	50	Sb	500
Co	500	Tl	2000
Cr	200	V	500
Cu	250	Zn	500

Table based on a final volume of 100 mL for water digests, and 200 mL for soil digests.

GRAPHITE FURNACE SPIKES

- Add the analytes listed in the table below to a 100 mL volumetric flask which contains ~50 mL of Type II water and 5 mL of HNO_3.

Analyte	Volume	Stock Concentration
As	400 µL	1000 ppm
Pb	200 µL	1000 ppm
Se	100 µL	1000 ppm
Tl	500 µL	1000 ppm

- Dilute to 100 mL with Type II water. This spike solution now contains:

4.0 ppm	Arsenic
2.0 ppm	Lead
1.0 ppm	Selenium
5.0 ppm	Thallium

- Add 1000 µL of Spike Solution to water samples and 2000 µL to soil samples prior to digestion.

ICP
CLP-LOW SPIKES

- Add the analytes from the two tables below into separate 100 mL volumetric flasks which contain ~50 mL of Type II water and 5 mL of HNO_3.

ICP-1

Analyte	Volume	Stock Concentration	Spike Concentration
Sb	500 µL	1000 ppm	5 ppm
Al	5000 µL	1000 ppm	50 ppm
Ba	2000 µL	1000 ppm	20 ppm
Be	100 µL	1000 ppm	1 ppm
Cr	500 µL	1000 ppm	5 ppm
Co	1000 µL	1000 ppm	10 ppm
Cu	500 µL	1000 ppm	5 ppm
Fe	2500 µL	1000 ppm	25 ppm
Mn	500 µL	1000 ppm	5 ppm
Ni	1000 µL	1000 ppm	10 ppm
V	1000 µL	1000 ppm	10 ppm
Zn	1000 µL	1000 ppm	10 ppm

ICP-2

Analyte	Volume	Stock Concentration	Spike Concentration
Ag	500 µL	1000 ppm	5 ppm

- Add 1000 µL of ICP-1 and 1000 µL of ICP-2 spike solutions to water samples prior to digestion. For soil samples, add 2000 µL of each spike solution prior to digestion. The final digest will contain:

Analyte	Concentration in Digest	Analyte	Concentration in Digest
Sb	50 ppb	Al	500 ppb
Ba	200 ppb	Be	10 ppb

Cr	50 ppb	Co	100 ppb
Cu	50 ppb	Fe	250 ppb
Mn	50 ppb	Ni	100 ppb
V	100 ppb	Zn	100 ppb
Ag	50 ppb		

Table based on final volume of 100 mL for water digests, and 200 mL for soil digests.

GRAPHITE FURNACE
CLP-LOW SPIKES

- Add the analytes listed in the table below to a 100 mL volumetric flask which contains ~50 mL of Type II water.

Analyte	Volume	Stock Concentration	Spike Concentration
As	100 µL	1000 ppm	1000 ppb
Se	500 µL	1000 ppm	5000 ppb
Tl	500 µL	1000 ppm	5000 ppb
Pb	250 µL	1000 ppm	2500 ppb
Cd	100 µL	1000 ppm	1000 ppb

- Add 1000 µL of Spike Solution to water samples and 2000 µL to soil samples prior to digestion. The final digest will contain*:

10 ppb Arsenic
50 ppb Selenium
50 ppb Thallium
25 ppb Lead
10 ppb Cadmium

*Based on 100 mL final volume for water digests and 200 mL for soil digests.

PDCA
SPIKES and LCSW

The LCSW for the PDCA extraction was make by adding 10 mL SPEX ICV-1™ solution to 100 mL of Type II water prior to extraction. The spike was made by adding 1000 µL of CLP SPK solution to a 100 mL aliquot of the sample prior to extraction.

ICP Analytes

Analyte	Concentration in Digest	Analyte	Concentration in Digest
Cd	50 ppb	Mn	500 ppb
Co	500 ppb	Ni	500 ppb
Cu	250 ppb	Ag	50 ppb
Fe	1000 ppb	V	500 ppb
Zn	500 ppb		

Graphite Furnace Analytes

Analyte	Concentration in Digest	Analyte	Concentration in Digest
Pb	500 ppb	Tl	2000 ppb
Se	2000 ppb		

Tables based on a final volume of 100 mL.

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STANDARDS LOGBOOK

#	ANALYTE	ID or STOCK No.	STOCK CONC.	VOL/WT TAKEN	FINAL VOL.	CONC.	SOLVENT	PREP. DATE	INIT.	EXP. DATE	QC'D (Initials)
1	CLP.SPK	ME1.03.06 EXP 12/12/96	(CLPP SPK 1)	10mL	100mL		5% HNO_3 H_2O	03/28/96	RJH	12/12/96	
		ME1.03.07 EXP 12/12/96	(CLPP.SPK2)								
		ME1.03.01 EXP 12/12/96	(CLPP.SPK3)								
2	GF-CAL1 (Pb)	ME3.86.09 EXP. 7/10/96	1000 g	30µL	100mL	0.3 ppm	0.5% HNO_3 H_2O	03/28/96	RJH	05/30/96	
	(Se)	ME3.86.10 EXP 7/10/96		50µL		0.5 ppm					
	(As)	ME3B1.9 EXP 5/30/96		100µL		1.0 ppm					
	(Tl)	ME3.86.11 EXP 7/10/96		100µL		1.0 ppm					
3	GF-CAL2 (Pb)	ME3.86.09 EXP 7/10/96	1000 g	100µL	100mL	1.0 ppm	0.5% HNO_3 H_2O	03/28/96	RJH	05/30/96	
	(Se)	ME3.86.10 EXP 7/10/96		100µL		1.0 ppm					
	(As)	ME3B1.9 EXP 5/30/96		250µL		2.5 ppm					
	3/28/96 RJH										

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

Method #: LTL-7010

Title: **Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy by SW846 Method 3010A**

Revision history:

Number	Date
1.	12/14/94
2.	06/03/96

UNCONTROLLED

Written by: Lucas Hawkins, Chemist — Date: 6/4/96

Reviewed by: Mark Strongman, Metals Supervisor — Date: 6.3.96

Reviewed by: Bill Lundberg, Inorganic Division Manager — Date: 6/4/96

Reviewed by: Harry Romberg, QC Officer — Date: 6-4-96

Approved by: Karen Kotz, Laboratory Director — Date: 6/4/96

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1. Introduction and Scope

1.1 This digestion procedure is used for the preparation of aqueous samples, TCLP and mobility-procedure extracts, and wastes that contain suspended solids for analysis by flame atomic absorption spectroscopy (FLAA) or inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

1.2 Samples prepared by Method 3010A may be analyzed by FLAA or ICP for the following:

Aluminum	Calcium	Magnesium	*Silver
*Antimony (also GFAA)	Chromium	Manganese	Sodium
**Arsenic	Cobalt	Molybdenum	Thallium
Barium	Copper	Nickel	*Tin (FLAA only)
Beryllium	Iron	Potassium	Vanadium
Cadmium	Lead	**Selenium	Zinc

* Although Antimony, Silver and Tin are not listed in the original SW846 document as analytes that may be analyzed from samples prepared by Method 3010A, Laucks has demonstrated adequate recovery for these analytes from this digestate. In addition, Laucks has demonstrated adequate Antimony recovery in samples prepared by LTL-7010 and analyzed by GFAA.

** Analysis by ICP

1.3 With the exception of Antimony, this digestion procedure is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy because hydrochloric acid can cause interference during furnace atomization. Consult Method LTL-7008 for samples requiring graphite furnace analysis.

2. Summary of Method

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If a sample goes to dryness, it must be discarded and prepared again.

3. Safety Procedures

3.1 These procedures involve the use of strong and/or hot acid solutions. The analyst must wear eye protection, a lab coat, and gloves to protect against burns.

3.2 These procedures involve hot plates which may present the danger of burns from heated surfaces and electrical hazards. The analyst must take appropriate caution to avoid injury from these sources.

3.3 Samples and spiking solutions may contain high levels of toxic metals and other unknown constituents. The analyst must take every precaution to avoid contact with these potentially hazardous materials and should wash hands thoroughly before eating or going home for the day.

4. Equipment

- 150-mL beakers or equivalent, acid-washed
- 100-mL graduated cylinder, acid-washed
- Ribbed watch glasses, acid-washed
- Eppendorf or other micropipets
- Hot plate or equivalent heating source, one that is adjustable and capable of maintaining a temperature of 90-95° C.
- Glass funnels, acid-washed
- Filter paper, Whatman No. 41 or equivalent
- Sample digestate bottles, acid-washed
- Thermometer

Note: All glassware used for this digestion must be prepared by the method stated in Inorganics Glass Cleaning Procedures, LTL-7003.

5. Reagents

5.1 Reagent Water. Reagent water will be interference-free. All references to water in the method refer to reagent water unless otherwise specified.

5.2 Nitric acid (concentrated), HNO_3, ACS Reagent grade or better.

5.3 Hydrochloric acid (concentrated), HCl, ACS Reagent grade or better.

The method blank, prepared along with the samples, is used as a contamination check. Since the holding time for all analytes associated with this method have a holding time of 6 months, repreparation would not be an issue if contamination was traced to a specific reagent.

6. Acid Digestion Procedure

See Appendix A for digestion log.
See Appendix B for flowchart.
See Appendix C for Quality Control solutions.

6.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL beaker and add 3 mL of concentrated HNO_3. If only one graduated cylinder is used for all samples, the preparation blank is to be the last sample dispensed to assure the absence of sample carry-over. Cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and carefully evaporate to 5 mL, making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Place a thermometer into a beaker of water on the hotplate. Record the temperature achieved during the digest on the digest log. Cool the beaker and add another 3-mL aliquot of HNO_3. Return the covered beaker to the hot plate and adjust the temperature, if necessary, so that a gentle reflux action occurs.

6.2 Continue heating, adding additional HNO_3 as necessary until the digestion is complete, indicated when the digestate is light in color or does not change in appearance upon additional heating. Evaporate the samples to 3 mL, not allowing any portion of the bottom of the beaker to go dry. After allowing the beakers to cool, add 5 mL of concentrated HCl and 5 mL reagent water. Reflux the samples for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

Note: If a sample is allowed to go to dryness at any stage of the digestion procedure, low recoveries will result. The sample must be discarded and prepared again.

6.3 After cooling the beakers, add 5mL concentrated HCl to obtain a final acid concentration of approximately 10%. Pour each sample into a 100-mL graduated cylinder, rinsing the beaker walls with water and adding the rinsate to the graduated cylinder, and bring to a final volume of 100 mL. If one graduated cylinder is to be used to adjust volume of each sample, the blank is to be the last sample dispensed. If silicates or other insoluble material that could clog the nebulizer are present in the samples, the samples should be allowed to settle overnight prior to analysis. Filtration should be performed only if there is concern that the insoluble material will not settle out of solution. Filter and dilute the samples to a final volume of 100 mL, using acid-washed filter apparatus to avoid sample contamination. Samples should be stored in acid-washed digestate bottles.

6.4 The prepared samples are then transferred to the metals analysis department. The digestion log is to reflect the time at the start and finish of the digest. In order to maintain strict chain of custody, the time and date when the digestates are relinquished to the analysis department, as well as the initials of the analyst accepting the digest, are recorded on the digestion log.

7. Quality Control

7.1 In each batch or SDG consisting of no more than 20 samples, a preparation blank is created. This consists of 100 mL of reagent water and the appropriate amounts of nitric and hydrochloric acid, digested in exactly the same way as the samples. If only one graduated cylinder is used for all samples, the preparation blank is to be the last sample

dispensed to assure the absence of sample carry-over. The blank should be labeled on the digestate bottle in the following way: B, date, instrument, S or W (for soil or water) and the sequence number of the digestion. Example: B111794ICPW01.

7.2 Spiked samples should be employed to determine accuracy. In each batch or SDG consisting of no more than 20 samples, either matrix spike / sample duplicate (MS/Dup) or matrix spike / matrix spike duplicate (MS/MSD) samples will be prepared. For SW846-specified quality control measures, MS/Dup samples will be prepared in the following way. Dispense one sample in triplicate. Two will be digested exactly as any other sample. The third must be spiked with the appropriate spike solutions determined by the analyst, and then treated as any other sample. All glassware and digestate bottles must be marked appropriately. If MS/MSD samples are required instead of the SW846-specified MS/Dup, both the second and third aliquots must be spiked and all glassware and digestate bottles marked appropriately.

7.3 Determine the analytes required for analysis by consulting sample work order information. Each spiking solution is given its own unique number according to the page and line of the standards logbook which it is entered into. This number and the volume dispensed must be clearly recorded on the digestion log. A sample page from the standards logbook is included in Appendix C.

7.4 In each batch or SDG consisting of no more than 20 samples, either a Blank Spike (BLK SPK) or a Laboratory Control Sample (ICP LCSW) must be digested in exactly the same manner as a sample. A Blank Spike consists of 100 mL of reagent water spiked at the levels determined by the analyst as outlined in Section 7.3.

8. References

8.1 USEPA, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, USEPA SW846, most recent version, Method 3010A.

Appendix A, Sample LTL-7010 Digestion Logs

LAUCKS TESTING LABORATORIES, INC.					ICP DIGESTION LOG				Place a √ in the box next to the method performed.			
SDG #:	Digest start : date/time				Digest finish : date/time				SW-846 3010A		CLP-water	
Analyst:	/				/				SW-846 3050A		CLP-soil	

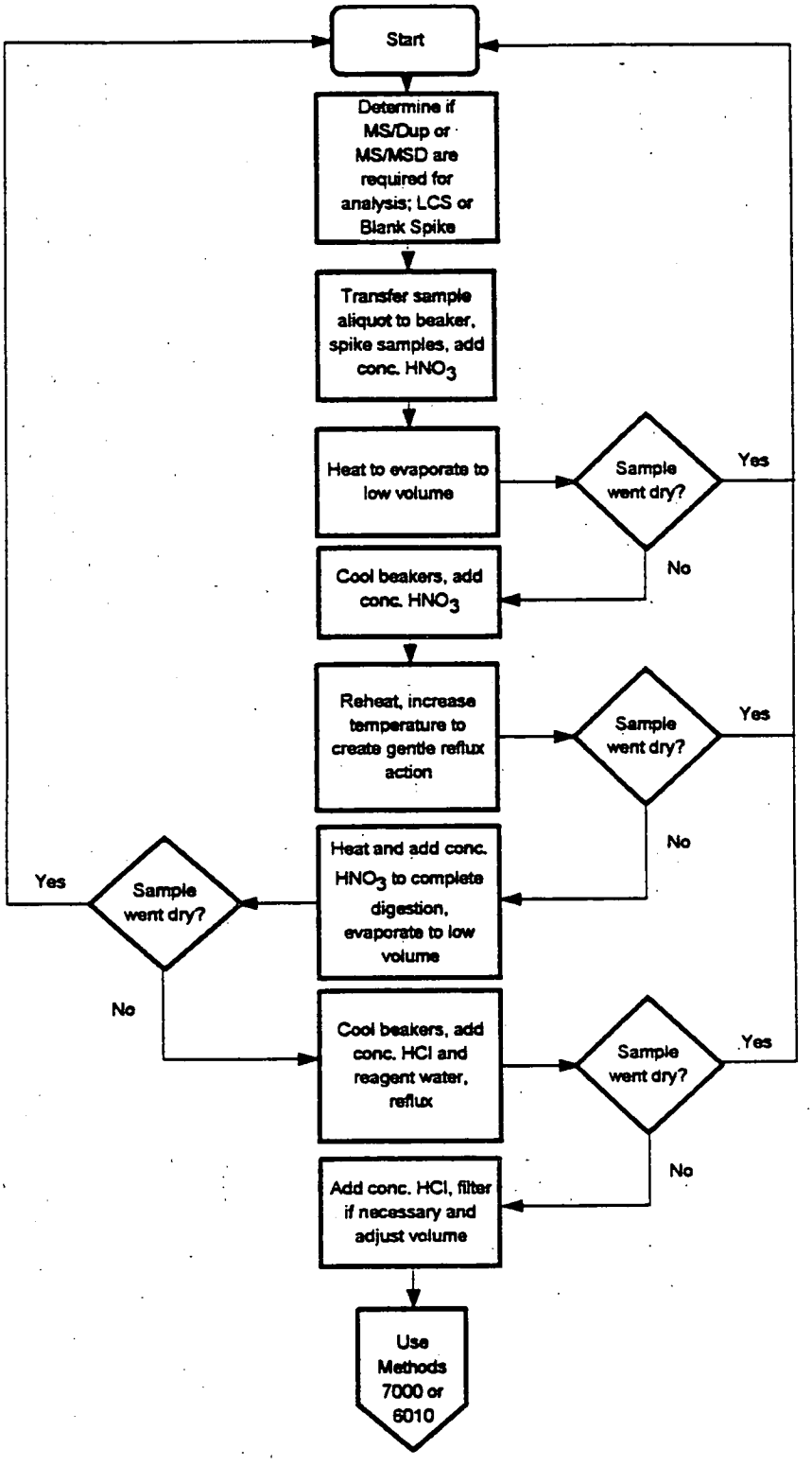
Sample ID	Sample Size (g:mL)	Final Volume (mL)	Color		Clarity		Text	Art	Comments
			Bef	Aft	Bef	Aft			

Chain of Custody	Digest Relinquished Date / Time : Analyst	Digest Accepted Analyst	Digest Disposed Date	Hot Plate Temperature, °C
	/			

Color 1=Red, 2=Blue, 3=Yellow, 4=Green, 5=Orange, 6=Violet, 7=White, 8=Brown, 9=Grey, 10=Black, 11=Colorless
Clarity 1=Clear, 2=Cloudy, 3=Opaque
Texture F=Fine (powdery), M=Medium (sandy), C=Coarse (rocky) Artifacts: If "Yes", give description in the comments field.

P:\METALS\BNCHSHEEP\DIG.D

Appendix B, Flowchart for LTL-7010


Start
Determine if MS/Dup or MS/MSD are required for analysis; LCS or Blank Spike
Transfer sample aliquot to beaker, spike samples, add conc. HNO_3
Heat to evaporate to low volume
Sample went dry?
Yes
No
Cool beakers, add conc. HNO_3
Reheat, increase temperature to create gentle reflux action
Sample went dry?
Yes
No
Heat and add conc. HNO_3 to complete digestion, evaporate to low volume
Sample went dry?
Yes
No
Cool beakers, add conc. HCl and reagent water, reflux
Sample went dry?
Yes
No
Add conc. HCl, filter if necessary and adjust volume
Use Methods 7000 or 6010

Appendix C, Quality Control Solutions

ICP LCSW

The LCSW for the ICP digest was made by diluting 100 mLs of SPEX ICV-1™ solution to 1000 mLs with type II water. A 100 mL aliquot of this solution was then digested.

ICP Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
Al	20000	Pb	500
Ba	20000	Mg	500000
Be	500	Mn	1500
Cd	500	Ni	4000
Ca	500000	K	500000
Cr	1000	Ag	1000
Co	5000	Na	500000
Cu	2500	V	5000
Fe	10000	Zn	2000
Sb	6000		

Other Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
As	1000	Tl	1000
Se	500		

Tables based on a final volume of 100 mL.

ICP Spikes

- The CLP spike solution for ICP digest was made by diluting 10 mLs of CLPP-SPK-1™, 10 mLs of CLPP-SPK-2™, and 10 mLs of CLPP-SPK-3™ to 100 mLs with Type II water.

- Add 1000 µLs of CLP spike solution to water samples and 2000 µLs of CLP spike solution to soil samples prior to digestion.

ICP Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
Ag	50	Fe	1000
Al	2000	Mn	500
As	2000	Ni	500
Ba	2000	Pb	500
Be	50	Se	2000
Cd	50	Sb	500
Co	500	Tl	2000
Cr	200	V	500
Cu	250	Zn	500

Table based on a final volume of 100 mL for water digests, and 200 mL for soil digests.

ICP
CLP-LOW SPIKES

- Add the analytes from the two tables below into separate 100 mL volumetric flasks which contain ~50 mL of Type II water and 5 mL of HNO_3.

ICP-1

Analyte	Volume	Stock Concentration	Spike Concentration
Sb	500 µL	1000 ppm	5 ppm
Al	5000 µL	1000 ppm	50 ppm
Ba	2000 µL	1000 ppm	20 ppm
Be	100 µL	1000 ppm	1 ppm
Cr	500 µL	1000 ppm	5 ppm
Co	1000 µL	1000 ppm	10 ppm
Cu	500 µL	1000 ppm	5 ppm
Fe	2500 µL	1000 ppm	25 ppm
Mn	500 µL	1000 ppm	5 ppm
Ni	1000 µL	1000 ppm	10 ppm
V	1000 µL	1000 ppm	10 ppm
Zn	1000 µL	1000 ppm	10 ppm

ICP-2

Analyte	Volume	Stock Concentration	Spike Concentration
Ag	500 µL	1000 ppm	5 ppm

- Add 1000 µL of ICP-1 and 1000 µL of ICP-2 spike solutions to water samples prior to digestion. For soil samples, add 2000 µL of each spike solution prior to digestion. The final digest will contain:

Analyte	Concentration in Digest	Analyte	Concentration in Digest
Sb	50 ppb	Al	500 ppb
Ba	200 ppb	Be	10 ppb
Cr	50 ppb	Co	100 ppb
Cu	50 ppb	Fe	250 ppb
Mn	50 ppb	Ni	100 ppb
V	100 ppb	Zn	100 ppb
Ag	50 ppb		

Table based on final volume of 100 mL for water digests, and 200 mL for soil digests.

PDCA
SPIKES and LCSW

The LCSW for the PDCA extraction was make by adding 10 mL SPEX ICV-1™ solution to 100 mL of Type II water prior to extraction. The spike was made by adding 1000 µL of CLP SPK solution to a 100 mL aliquot of the sample prior to extraction.

ICP Analytes

Analyte	Concentration in Digest	Analyte	Concentration in Digest
Cd	50 ppb	Mn	500 ppb
Co	500 ppb	Ni	500 ppb
Cu	250 ppb	Ag	50 ppb
Fe	1000 ppb	V	500 ppb
Zn	500 ppb		

Graphite Furnace Analytes

Analyte	Concentration in Digest	Analyte	Concentration in Digest
Pb	500 ppb	Tl	2000 ppb
Se	2000 ppb		

Tables based on a final volume of 100 mL.

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#	ANALYTE	ID or STOCK No.	STOCK CONC.	VOL/WT TAKEN	FINAL VOL.	CONC.	SOLVENT	PREP. DATE	INIT.	EXP. DATE	QC'D (Initials)
1	CLP.SPK	ME1.03.06 EXP 12/12/96	(CLPP.SPK1)	10mL	100mL		5% HNO_3 H_2O	03/28/96	RJH	12/12/96	
		ME1.03.07 EXP 12/12/96	(CLPP.SPK2)								
		ME1.03.01 EXP 12/12/96	(CLPP.SPK3)								
2	GF-CAL1 (Pb)	ME3.86.09 EXP. 7/10/96	1000 g	30µL	100mL	0.3 ppm	0.5% HNO_3 H_2O	03/28/96	RJH	05/30/96	
	(Se)	ME3.86.10 EXP 7/10/96		50µL		0.5 ppm					
	(As)	ME3.81-9 EXP 5/30/96		100µL		1.0 ppm					
	(Tl)	ME3.86.11 EXP 7/10/96		100µL		1.0 ppm					
3	GF-CAL2 (Pb)	ME3.86.09 EXP 7/10/96	1000 g	100µL	100mL	1.0 ppm	0.5% HNO_3 H_2O	03/28/96	RJH	05/30/96	
	(Se)	ME3.86.10 EXP 7/10/96		100µL		1.0 ppm					
	(As)	ME3.81.9 EXP 5/30/96		250µL		2.5 ppm					
	3/28/96 RJH										

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP: LTL-7012

Title: **Microwave Assisted Acid Digestion of Sediments, Sludge, Soils, and Oils Using SW846 Method 3051**

Revision history:

Number	Date
0.	6/04/96
1.	8/21/98

UNCONTROLLED

Revised by: _____ Date: 08-21-98
Ming-Hwa Hwang, Metals Supervisor

Reviewed by: Harry Romberg Date: 8-21-98
Harry Romberg, QA Officer

Approved by: Kathy Kreps Date: 8-24-98
Kathy Kreps, Laboratory Director

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1. Introduction and Scope

1.1 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 This digestion procedure is used for the preparation of sediments, sludge, soils, and oils for analysis by flame atomic absorption spectroscopy (FLAA), graphite furnace absorption spectroscopy (GFAA), inductively coupled argon plasma spectroscopy (ICP), or inductively coupled argon plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determination of available metals.

1.3 Samples prepared by Method 3051 using nitric acid digestion may be analyzed by FLAA, GFAA, ICP or ICP-MS for the following:

Aluminum	Cadmium	Iron	Molybdenum	Sodium
Antimony	Calcium	Lead	Nickel	Strontium
Arsenic	Chromium	Magnesium	Potassium	Thallium
Boron	Cobalt	Manganese	Selenium	Vanadium
Barium	Copper	Mercury	Silver	Zinc
Beryllium				

1.4 This method is provided as an alternate to LTL-7011. It is intended to provide a rapid multielement acid leach digestion prior to analysis by Flame Atomic Absorption(FLAA), Graphite Furnace Atomic Absorption(GFAA), Inductively Coupled Plasma Emission Spectroscopy, or Inductively Coupled Plasma Mass Spectroscopy(ICP-MS). If a decomposition including Hydrochloric Acid is required for certain elements, it is recommended that LTL-7011 be used. The parameters which are quoted in this procedure are those recommended by the manufacturer of the microwave digestion system used, in order to be in compliance with SW-846 protocols.

2. Summary of Method

2.1 A representative sample of up to 0.5g is digested in a Teflon vessel with 10 mL of HNO_3 in a microwave unit. After cooling, the vessel contents are either filtered or allowed to settle and diluted to volume and analyzed by an appropriate method.

3. Safety Procedures

3.1 These procedures involve the use of strong and/or hot acid solutions. The analyst must wear eye protection, a lab coat, and gloves to protect against burns.

3.2 Samples and spiking solutions may contain high levels of toxic metals and other unknown constituents. The analyst must take every precaution to avoid contact with these potentially hazardous materials and should wash hands thoroughly before eating or leaving the laboratory.

3.3 **Very reactive or volatile materials may create high pressures when heated, causing the vessels to vent with potential loss of sample and analytes. Samples that contain carbonates or other carbon dioxide generating compounds may generate enough pressure to vent the vessel. If this situation is anticipated the analyst may wish to use a smaller sample or an alternative digestion method.**

4. Equipment

- MDS-2100 Microwave Digestion system, CEM
- 120 mL Teflon® vessels and caps, carousel
- 50 or 100 mL graduated cylinder, acid washed
- Glass funnels, acid-washed
- Filter paper, Whatman No. 41 or equivalent
- Sample digestate bottles, acid washed
- Analytical balance, capable of weighing ± 0.01 g

Note: All glassware used for this digestion must be prepared by the method stated in Inorganics Glassware Cleaning Procedures, LTL-7003.

All Teflon® vessels and caps are to be thoroughly rinsed with deionized water prior to digestions and shaken to remove any significant droplets in the vessels.

The microwave is to be calibrated according to the procedures stated in SW846 method 3051. The MDS-2100 microwave, being designed with temperature control, does not require the calibration outlined in method 3051.

5. Reagents

5.1 Reagent Water - Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified.

5.2 Nitric acid (concentrated), HNO_3, ACS Reagent grade or better. Acid should be analyzed to determine levels of impurities. If the method blank is less than reporting limit then the acid can be used.

6. Microwave Sample Digestion Procedure

See Appendix A for digestion log
See Appendix B for flowchart
See Appendix C for quality control solutions

6.1 Weigh a well mixed sample directly into the Teflon digestion vessel to the nearest 0.01g. For soils, sludge and sediments, use no more than 0.50g. For oils, use no more than 0.25g.

6.2 Add 10 mL of concentrated nitric acid to each vessel and cap hand tight. If a vigorous reaction occurs with the addition of the acid, wait for the reaction to subside before capping. For each microwave digestion run, the pressure control lid is to accompany the sample that seems to have the most carbon. Weigh each capped vessel to the nearest 0.01 g.

6.3 Microwave

6.3.1 MDS-2100 Microwave Digestion system, CEM

6.3.2 Place the carousel in the unit and attach the pressure control line to the digestion vessel with the double ported lid. Run the heating program SW-3051 (temperature).

Program SW-3051 (temperature) as follows:

Stage	(1)	(2)	(3)	(4)	(5)
%POWER	100	0	0	0	0
PSI	70	0	0	0	0
RAMP	05:00	0000	0000	0000	0000
HOLD	04:30	0000	0000	0000	0000
TEMP	175	000	000	000	000

6.4 At the end of the microwave program, allow the vessels to cool in the unit for a minimum of 5 minutes before removal to avoid possible injury if a vessel vents immediately after microwave heating. Once they are at room temperature, weigh and record the weight of each vessel assembly. If the weight of the sample plus acid has decreased by more than 10%, discard and prepare the sample again.

6.5 Uncap the vessels in a fume hood due to the likely presence of nitrogen oxide. Dilute sample to 50 mL in a graduated cylinder and transfer the samples to an acid-cleaned polyethylene bottle. If only one graduated cylinder is used to volume all samples, the blank is to be the final sample diluted to assure the absence of sample carry-over. If the digested sample contains particulate which may clog nebulizers or interfere with injection of the sample into an instrument, the sample may be allowed to settle or be filtered.

6.6 The prepared samples are then transferred to the metals analysis department. The digestion log is to reflect the time at the start and finish of the digest. In order to maintain a strict chain of custody, the time and date when the digestates are relinquished to the analysis department, as well as the initials of the analyst accepting the digest, are recorded on the digestion log

7. Quality Control

7.1 In each batch or SDG consisting of no more than 20 samples, a preparation blank is created. The blank should be labeled on the digestate bottle in the following way: B, date, M (microwave), S (soil) and the sequence number of the digestion. Example B061598MS01.

7.2 Spiked samples should be employed to determine accuracy. In each batch or SDG consisting of no more than 20 samples, either matrix spike / sample duplicate (MS/Dup) or matrix spike /matrix spike duplicate (MS/MSD) samples will be prepared. For SW3051-specified quality control measures, MS/Dup samples will be prepared in the following way. Dispense a sample in triplicate. Two will be analyzed exactly as any other sample. The third must be spiked with the appropriate spike solutions, determined by the analyst. All glassware and digestate bottles must be marked appropriately. If MS/MSD samples are required instead of the SW846-specified MS/Dup, both the second and third aliquot must be spiked.

7.3 Determine the analytes required for analysis by consulting sample work order information. The analyst must record the specific spiking solution(s) used, the volume(s) of the solution(s), and the corresponding Metals Standard Logbook number(s) on the digestion log as illustrated in Appendix C

7.4 In each batch or SDG consisting of no more than 20 samples, prepare a Lab Control Sample (LCSS) in exactly the same manner as a sample. All spikes and standard reference materials must be recorded by the analyst on the digestion log. The record must state the specific spiking solution used, the volume of the solution, and it's Metals Standard Logbook number, and the lot number of any reference materials.

8. References

8.1 USEPA, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, USEPA SW846, most recent version, Method 3051.

Appendix A, Sample LTL-7012 Digestion Logs

Laucks Testing Laboratories, INC.	START DATE TIME	FINISH DATE TIME	METHOD	ANALYST	ANALYSIS
SDG #:			SW846 3051		Microwave Digestion
MATRIX: SOIL					

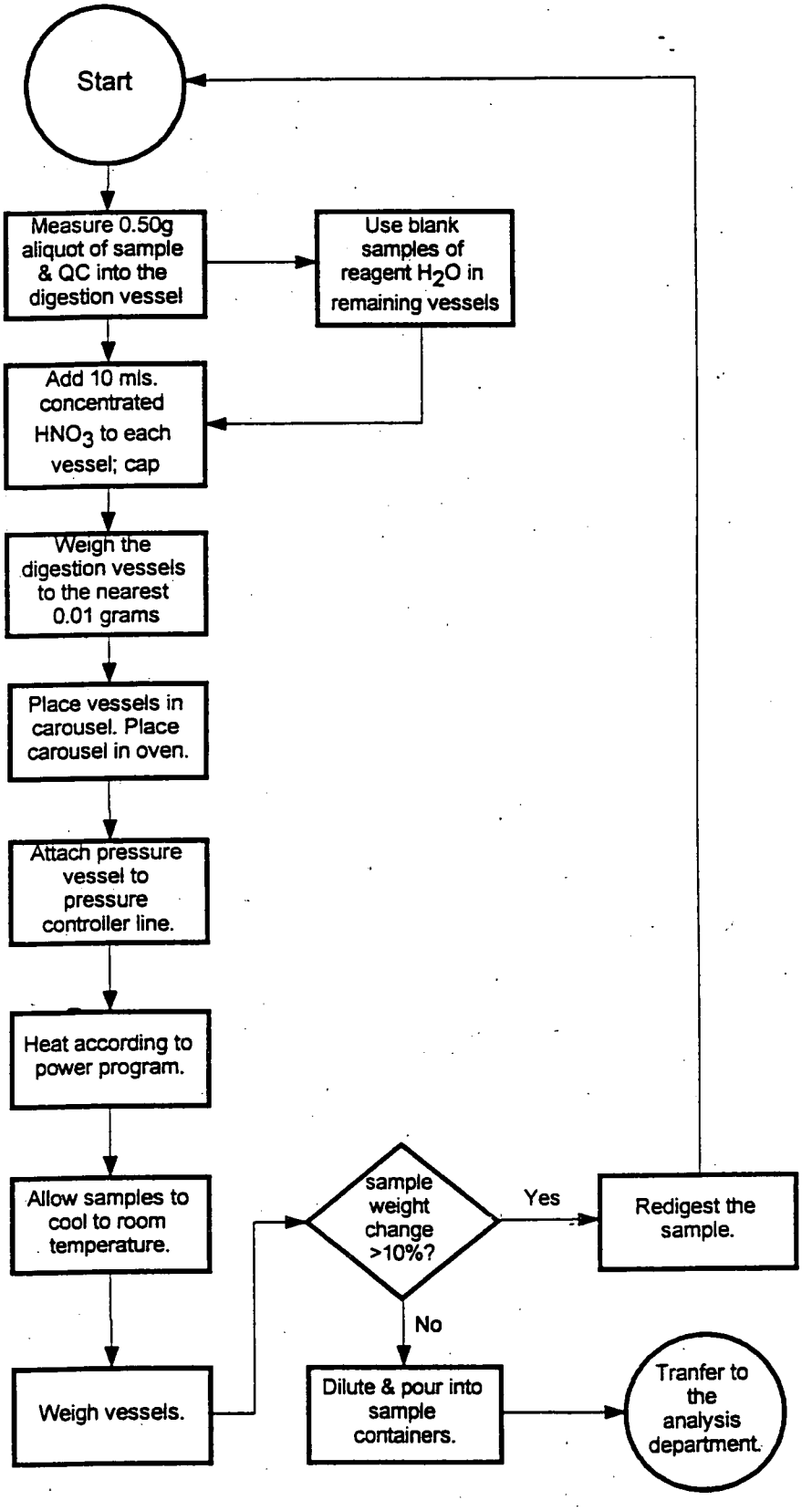
Bomb #	Sample ID	Samp (g)	Final Vol (mL)	Color		Text	Artifacts	Bomb & Sample (g)	Final Bomb (g)	Δ (g)	Δ >0.5 g?
				Int	Fin						

Chain of Custody	Digest Relinquished Date / Time : Analyst	Digest Accepted :Analyst	Digest Disposed :Date
	/ :		

COLOR: 1 = Red, 2 = Blue, 3 = Yellow, 4 = Green, 5 = Orange, 6 = Violet, 7 = White, 8 = Brown, 9 = Gray, 10 = Black, 11 = Colorless.

TEXTURE: F = Fine (Powdery), M = Medium (Sandy), C = Coarse (Rocky).

Appendix B, Flowchart for LTL-7012


Start
Measure 0.50g aliquot of sample & QC into the digestion vessel
Use blank samples of reagent H_2O in remaining vessels
Add 10 mls. concentrated HNO_3 to each vessel; cap
Weigh the digestion vessels to the nearest 0.01 grams
Place vessels in carousel. Place carousel in oven.
Attach pressure vessel to pressure controller line.
Heat according to power program.
Allow samples to cool to room temperature.
Weigh vessels.
sample weight change >10%?
Yes
Redigest the sample.
No
Dilute & pour into sample containers.
Tranfer to the analysis department.

Appendix C, Quality Control Solutions

ICP Spikes

- The CLP spike solution for ICP digest was made by diluting 10 mLs of CLPP-SPK-1™, 10 mLs of CLPP-SPK-2™, and 10 mLs of CLPP-SPK-3™ to 100 mLs with Type II water.

- Add 500 µLs of CLP spike solution to soil samples prior to digestion.

ICP Analytes

Analyte	Concentration in Digest (µg/L)	Analyte	Concentration in Digest (µg/L)
Ag	50	Fe	1000
Al	2000	Mn	500
As	2000	Ni	500
Ba	2000	Pb	500
Be	50	Se	2000
Cd	50	Sb	500
Co	500	Tl	2000
Cr	200	V	500
Cu	250	Zn	500

Table based on a final volume of 50 mL for soil digests.

GRAPHITE FURNACE SPIKES

- Add the analytes listed in the table below to a 100 mL volumetric flask which contains ~50 mL of Type II water and 5 mL of HNO_3.

Analyte	Volume	Stock Concentration
As	400 µL	1000 mg/L
Pb	200 µL	1000 mg/L
Se	100 µL	1000 mg/L
Tl	500 µL	1000 mg/L

- Dilute to 100 mL with Type II water. This spike solution now contains:

4.0 mg/L	Arsenic
2.0 mg/L	Lead
1.0 mg/L	Selenium
5.0 mg/L	Thallium

- Add 500 µL of Spike Solution to soil samples prior to digestion.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

Method #: LTL-7015

Title: **Acid Digestion of Sediments, Sludge, and Soils by SW846 Method 3050B**

Revision history:

Number	Date
0.0	1/18/99
1.0	3/20/00

Controlled Document
No. 20 Assigned to: Tetra

Revised by: Stan Dittrick — Date: 3/20/00
Stan Dittrick, Chemist

Reviewed by: Paul Swift — Date: 03/21/2000
Paul Swift, Inorganic Division Manager

Reviewed by: Harry Romberg — Date: 3-20-2000
Harry Romberg, QA Officer

Written by: Kathy Kreps — Date: 03-22-2000
Kathy Kreps, Laboratory Director

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1. Introduction and Scope

1.1. This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP) or inductively coupled argon plasma spectroscopy - mass spectrometry (ICP-MS). Samples prepared by this method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below (see also step 2.1):

FLAA/ICP-AES		GFAA/ICP-MS
Aluminum	Magnesium	Arsenic
Antimony	Manganese	Beryllium
*Arsenic	Molybdenum	Cadmium
Barium	Nickel	Chromium
Beryllium	Potassium	Cobalt
Cadmium	*Selenium	Iron
Calcium	Silver	Lead
Chromium	Sodium	Molybdenum
Cobalt	Thallium	Selenium
Copper	*Tin (FLAA only)	*Tin (ICP-MS only)
Iron	Vanadium	Thallium
Lead	Zinc	

* Although Arsenic and Selenium (analyzed by FLAA/ICP) and Tin (analyzed by FLAA or ICP-MS) are not listed in the original SW846 document as analytes that may be analyzed from samples prepared by Method 3050B, Laucks has demonstrated adequate recovery for these analytes from this digestate.

2. Summary of Method

2.1 A representative 1. to 1.5g sample is digested in nitric acid and hydrogen peroxide. The digestate is then either reduced to a low volume or refluxed with hydrochloric acid. Hydrochloric acid is used for flame AA and ICP analyses only. Dilute hydrochloric acid is used as the final reflux acid for (1) the ICP analysis of As and Se, (2) the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sn, Tl, V, and Zn. The hydrochloric acid step is omitted for the furnace AA analysis of As, Be, Cd, Cr, Co, Fe, Pb, Mo, Se, and Tl. The diluted samples have an approximate acid concentration of 5% (v/v).

3. Safety Procedures

3.1 These procedures involve the use of strong and/or hot acid solutions. The analyst must wear eye protection, a lab coat, and gloves to protect against burns.

3.2. These procedures involve hot plates which may present the danger of burns from heated surfaces and electrical hazards. The analyst must take appropriate caution to avoid injury from these sources.

3.3. Samples and spiking solutions may contain high levels of toxic metals and other unknown constituents. The analyst must take every precaution to avoid contact with these potentially hazardous materials and should wash hands thoroughly before taking any breaks, eating, or going home for the day.

3.4. Fertilizer samples are chemically complex matrices and should be handled with extreme caution. Many components found in fertilizer are highly reactive to acid and all acid additions should be made with special care, in a hood, standing back from the sample. Also, these samples have been known to "pop" or explode during heating, so care should be taken not to stand close to or have any body part over the samples while they are being heated.

4. Equipment

- 250-mL Erlenmeyer flasks or equivalent, acid-washed
- Analytical balance capable of accurately weighing to the nearest 0.01 g
- Reflux caps fitted for Erlenmeyer flasks, acid-washed
- Eppendorf or other micropipets
- Hot plate or equivalent heating source, adjustable and capable of maintaining a temperature of 90-95° C
- 100-mL graduated cylinder, acid-washed

- Filter paper, Whatman No. 41 or equivalent
- Glass funnels, acid-washed
- 100-mL volumetric flasks, acid-washed
- Sample digestate bottles, acid-washed
- Thermometer

Note: All glassware used for this digestion must be prepared by the method stated in Inorganics Glass Cleaning Procedures, SOP #: LTL-7003.

5. Reagents

5.1 Reagent Water. Reagent water will be interference-free deionized water. All references to water in the method refers to reagent water unless otherwise specified.

5.2 Nitric acid (concentrated), HNO_3, ACS Reagent grade or better

5.3 Hydrochloric acid (concentrated), HCl, ACS Reagent grade or better

5.4 Hydrogen peroxide (30%), H_2O_2, ACS Reagent grade or better

The method blank prepared along with the samples is used as a contamination check. Since the holding time for all analytes associated with this method have a holding time of 6 months, repreparation would not be an issue if contamination was traced to a specific reagent.

6. Acid Digestion Procedure

See Appendix A for digestion logs.
See Appendix B for flowchart.
See Appendix C for Quality Control solutions
See Appendix D for Procedure Checklist

6.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh 1.00-1.50 g of sample to the nearest 0.01 g directly into an Erlenmeyer flask. For samples with low percent solids, a larger sample size may be used to attain the equivalent of 1.00-1.50 g dry basis as long as digestion is completed. Add appropriate spiking mix aliquots to QC samples at this point.

6.2 Place the reflux caps on the flasks, add 5 mL of concentrated HNO_3, 5 mL H_2O and mix the slurry. Heat the samples to 95° C and reflux without boiling for 15 minutes. Allow the samples to cool. Record the temperature in the digest log. Add 5 mL of concentrated HNO_3, heat 30 min and allow the samples to cool. If brown fumes are generated continue to add

acid, heat and cool until fumes are no longer emitted. Reflux the samples for two hours or allow them to evaporate to 5 mL with reflux caps. Allow the samples to cool.

6.3 Add 2 mL water, 3 mL 30% H_2O_2, heat for 10 minutes and cool the samples. Add 1 mL 30% H_2O_2, reflux for 10 minutes and allow the samples to cool. Repeat the addition of 1 mL H_2O_2 and heat until effervescence is minimal or a maximum of 10 mL H_2O_2 is added. Make sure that sample losses do not occur due to excessive effervescence. Reduce the sample to 5 mL.

6.4 If the sample is being prepared for GFAA or ICP-MS analysis then skip this step otherwise add 10 mL of concentrated HCl. Heat the sample for 15 minutes and allow it to cool.

6.5 Dilute the sample to 100 mL with water in a graduated cylinder and place in an acid-washed digestate bottle. If only one graduated cylinder is to be used to measure all samples, then bring the blank to volume after the rest of the samples. This will help to determine if their is any sample carry over contamination.

Note: If a sample is allowed to go dry at any stage of the digestion procedure, the sample must be discarded and redigested.

6.6 If silicates or other insoluble material that could clog the nebulizer or the graphite furnace autosampler are present in the samples, allow the samples to settle overnight prior to analysis. If there is concern that the insoluble material will not settle out of solution filter the sample with Whatman No. 41 or equivalent filter paper.

6.7 In the digestion log record the start date/time, finish date/time, and the date/time digestates are relinquished. Transfer the samples to the metals analysis department. Have the analyst accepting the digestates initial and date the digestion log

7. Quality Control

7.1 In each batch or SDG consisting of no more than 20 samples, a preparation blank is created. This consists of an empty, acid-washed Erlenmeyer flask to which the appropriate reagents are added and digested in exactly the same manner as a sample The blank should be labeled on the digestate bottle in the following way: B, date, instrument, S or W (for soil or water) and the sequence number of the digestion. Example: B111794ICPS01.

7.2 Spiked samples should be employed to determine accuracy. In each batch or SDG consisting of no more than 20 samples, either matrix spike / sample duplicate (MS/Dup) or matrix spike / matrix spike duplicate (MS/MSD) samples will be prepared. For SW846-

specified quality control measures, MS/Dup samples will be prepared in the following way. Dispense one sample in triplicate. Two will be digested exactly as any other sample. The third must be spiked with the appropriate spike solutions determined by the analyst, and then treated as any other sample. All glassware and digestate bottles must be marked appropriately. If MS/MSD samples are required instead of the SW846-specified MS/Dup, both the second and third aliquots must be spiked and all glassware and digestate bottles marked appropriately. See Appendix C for instructions on the preparation and use of QC solutions. Spiking levels presented are to be used only as guidance. The actual analytes and concentrations may vary.

7.3 Determine the analytes required for analysis by consulting sample work order information. Each spiking solution is given its own unique number according to the page and line of the standards logbook which it is entered into. This number and the volume dispensed must be clearly recorded on the digestion log. A sample page from the standards logbook is included in the Appendix C.

7.4 In each batch or SDG consisting of no more than 20 samples, either a Blank Spike (BLK SPK) or a Laboratory Control Sample (ICP or GF LCSS) must be digested in exactly the same manner as a sample. A Blank Spike consists of an empty, acid-washed Erlenmeyer flask to which the appropriate spikes (determined as outlined in Section 7.3) and reagents are added. The Certified Value and Advisory range for each analyte in a particular LCSS can be accessed from the Quality Control Database.

8. References

8.1 USEPA, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, USEPA SW846, most recent version, Method 3050B.

Appendix A, LTL-7015 Digestion Logs

LAUCKS TESTING LABORATORIES, INC.		ICP DIGESTION LOG	Place a √ in the box next to the method performed.		
	Digest start : date/time	Digest finish : date/time	SW-846 3005A		ILM04.0-water
SDG #:			SW-846 3010A		ILM04.0-soil
Analyst:			SW-846 3050A		SW-846 3050B

	Sample ID	Sample Size (g:mL)	Final Volume (mL)	Color		Clarity		Text	Art	Comments	Bottle #
				Bef	Aft	Bef	Aft				
01											
02											
03											
04											
05											
06											
07											
08											
09											
10											
11											
12											
13											
14											
15											
16											
17											
18											
19											
20											
21											
22											
23											
24											

Chain of Custody	Digest Relinquished Date / Time : Analyst	Digest Accepted Analyst	Digest Disposed Date	Hot Plate Temperature, °C

Reagents Lot Number	HNO_3	HCl	H_2O_2

Color 1=Red, 2=Blue, 3=Yellow, 4=Green, 5=Orange, 6=Violet, 7=White, 8=Brown, 9=Grey, 10=Black, 11=Colorless
Clarity 1=Clear, 2=Cloudy, 3=Opaque
P:\metals\bnchshee\icpdig.doc
Texture F=Fine (powdery), M=Medium (sandy), C=Coarse (rocky) Artifacts: If "Yes", give description in the comments field.

P:\metals\bnchshee\icpdig.doc

LAUCKS TESTING LABORATORIES, INC.		GRAPHITE FURNACE DIGESTION LOG	Place a √ in the box next to the method performed.		
	Digest start : date/time	Digest finish : date/time	SW-846 3020A		ILM04.0-water
SDG #:			SW-846-7060A		ILM04.0-soil
Analyst:			SW-846 3050A		SW-846 305

	Sample ID	Sample Size (g:mL)	Final Volume (mL)	Color		Clarity		Text	Art	Comments	Bottle #
				Bef	Aft	Bef	Aft				
01											
02											
03											
04											
05											
06											
07											
08											
09											
10											
11											
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20											
21											
22											
23											
24											

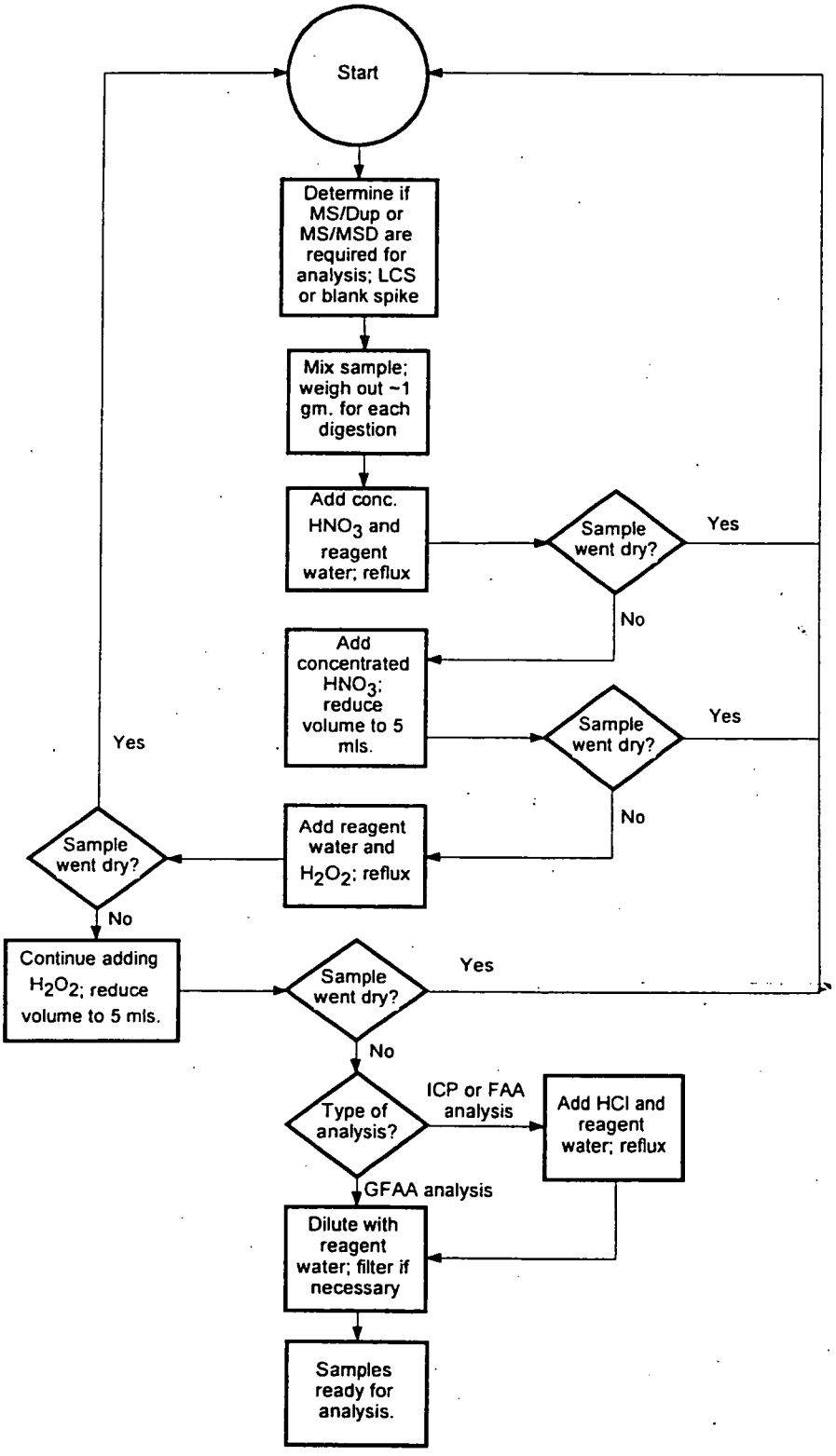
Chain of Custody	Digest Relinquished Date / Time : Analyst	Digest Accepted Analyst	Digest Disposed Date	Hot Plate Temperature, °C

Reagents Lot Number	HNO_3	HCl	H_2O_2

Color 1=Red, 2=Blue, 3=Yellow, 4=Green, 5=Orange, 6=Violet, 7=White, 8=Brown, 9=Grey, 10=Black, 11=Colorless
Clarity 1=Clear, 2=Cloudy, 3=Opaque
Texture F=Fine (powdery), M=Medium (sandy), C=Coarse (rocky) Artifacts: If "Yes", give description in the comments field.

P:\metals\benchsee\gfdig.doc

Appendix B, Flowchart for LTL-7015


Start
Determine if MS/Dup or MS/MSD are required for analysis; LCS or blank spike
Mix sample; weigh out ~1 gm. for each digestion
Add conc. HNO_3 and reagent water; reflux
Sample went dry?
Yes
No
Add concentrated HNO_3; reduce volume to 5 mls.
Sample went dry?
Yes
No
Add reagent water and H_2O_2; reflux
Sample went dry?
Yes
No
Continue adding H_2O_2; reduce volume to 5 mls.
Sample went dry?
Yes
No
Type of analysis?
ICP or FAA analysis
Add HCl and reagent water; reflux
GFAA analysis
Dilute with reagent water; filter if necessary
Samples ready for analysis.

Appendix C, Quality Control Solutions

ICP Spikes

- The CLP spike solution for ICP digest was made by diluting 10 mLs of CLPP-SPK-1™, 10 mLs of CLPP-SPK-2™, and 10 mLs of CLPP-SPK-3™ to 100 mLs with Type II water.

- Add 1000 µLs of CLP spike solution to water samples and 2000 µLs of CLP spike solution to soil samples prior to digestion.

ICP Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
Ag	50	Fe	1000
Al	2000	Mn	500
As	2000	Ni	500
Ba	2000	Pb	500
Be	50	Se	2000
Cd	50	Sb	500
Co	500	Tl	2000
Cr	200	V	500
Cu	250	Zn	500

Table based on a final volume of 100 mL for water digests, and 200 mL for soil digests.

GRAPHITE FURNACE SPIKES

- Add the analytes listed in the table below to a 100 mL volumetric flask which contains ~50 mL of Type II water and 5 mL of HNO_3.

Analyte	Volume	Stock Concentration
As	400 µL	1000 ppm
Pb	200 µL	1000 ppm
Se	100 µL	1000 ppm
Tl	500 µL	1000 ppm

- Dilute to 100 mL with Type II water. This spike solution now contains:

4.0 ppm	Arsenic
2.0 ppm	Lead
1.0 ppm	Selenium
5.0 ppm	Thallium

- Add 1000 µL of Spike Solution to water samples and 2000 µL to soil samples prior to digestion.

ICP
CLP-LOW SPIKES

- Add the analytes from the two tables below into separate 100 mL volumetric flasks which contain ~50 mL of Type II water and 5 mL of HNO_3.

ICP-1

Analyte	Volume	Stock Concentration	Spike Concentration
Sb	500 µL	1000 ppm	5 ppm
Al	5000 µL	1000 ppm	50 ppm
Ba	2000 µL	1000 ppm	20 ppm
Be	100 µL	1000 ppm	1 ppm
Cr	500 µL	1000 ppm	5 ppm
Co	1000 µL	1000 ppm	10 ppm
Cu	500 µL	1000 ppm	5 ppm
Fe	2500 µL	1000 ppm	25 ppm
Mn	500 µL	1000 ppm	5 ppm
Ni	1000 µL	1000 ppm	10 ppm
V	1000 µL	1000 ppm	10 ppm
Zn	1000 µL	1000 ppm	10 ppm

ICP-2

Analyte	Volume	Stock Concentration	Spike Concentration
Ag	500 µL	1000 ppm	5 ppm

- Add 1000 µL of ICP-1 and 1000 µL of ICP-2 spike solutions to water samples prior to digestion. For soil samples, add 2000 µL of each spike solution prior to digestion. The final digest will contain:

Analyte	Concentration in Digest	Analyte	Concentration in Digest
Sb	50 ppb	Al	500 ppb
Ba	200 ppb	Be	10 ppb

Cr	50 ppb	Co	100 ppb
Cu	50 ppb	Fe	250 ppb
Mn	50 ppb	Ni	100 ppb
V	100 ppb	Zn	100 ppb
Ag	50 ppb		

Table based on final volume of 100 mL for water digests, and 200 mL for soil digests.

GRAPHITE FURNACE
CLP-LOW SPIKES

- Add the analytes listed in the table below to a 100 mL volumetric flask which contains ~50 mL of Type II water.

Analyte	Volume	Stock Concentration	Spike Concentration
As	100 µL	1000 ppm	1000 ppb
Se	500 µL	1000 ppm	5000 ppb
Tl	500 µL	1000 ppm	5000 ppb
Pb	250 µL	1000 ppm	2500 ppb
Cd	100 µL	1000 ppm	1000 ppb

- Add 1000 µL of Spike Solution to water samples and 2000 µL to soil samples prior to digestion. The final digest will contain*:

10 ppb Arsenic
50 ppb Selenium
50 ppb Thallium
25 ppb Lead
10 ppb Cadmium

*Based on 100 mL final volume for water digests and 200 mL for soil digests.

ICP LCSW

The LCSW for the ICP digest was made by diluting 10 mLs of CLP-SPIKE and 50 mLs of LTL-6 solutions, and 2 mLs of conc. HNO_3 to 1000 mLs with type II water. A 100 mL aliquot of this solution was then digested.

ICP Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
Al	2000	Pb	500
Ba	2000	Mg	50000
Be	50	Mn	500
Cd	50	Ni	500
Ca	50000	K	50000
Cr	200	Ag	50
Co	500	Na	50000
Cu	250	V	500
Fe	1000	Zn	500
Sb	500		

Other Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
As	2000	Tl	2000
Se	2000		

Tables based on a final volume of 100 mL.

Graphite Furnace LCSW

- Add the analytes listed in the table below to a 100 mL volumetric flask which contains ~50 mL of Type II water and 2 mL of HNO_3. Dilute to volume with Type II water.

Analyte	Volume	Stock Concentration
As	500 µL	1000 ppm
Pb	500 µL	1000 ppm
Se	250 µL	1000 ppm
Tl	250 µL	1000 ppm
Cd	100 µL	1000 ppm

- Dilute to 100 mL with Type II water. This LCSW stock solution now contains:

5.0 ppm	Arsenic
5.0 ppm	Lead
2.5 ppm	Selenium
2.5 ppm	Thallium
1.0 ppm	Cadmium

The LCSW for the GFAA digest was made by diluting 10 mLs of LCSW stock solution and 20 mLs of conc. HNO_3 to 1000 mLs with type II water. A 100 mL aliquot of this solution was then digested.

Graphite Furnace Analytes

Analyte	Concentration in Digest (ppb)	Analyte	Concentration in Digest (ppb)
As	50	Tl	25
Pb	50	Cd	10
Se	25		

Tables based on a final volume of 100 mL.

PDCA
SPIKES and LCSW

The LCSW for the PDCA extraction was make by adding 10 mL SPEX ICV-1™ solution to 100 mL of Type II water prior to extraction. The spike was made by adding 1000 µL of CLP SPK solution to a 100 mL aliquot of the sample prior to extraction.

ICP Analytes

Analyte	Concentration in Digest	Analyte	Concentration in Digest
Cd	50 ppb	Mn	500 ppb
Co	500 ppb	Ni	500 ppb
Cu	250 ppb	Ag	50 ppb
Fe	1000 ppb	V	500 ppb
Zn	500 ppb		

Graphite Furnace Analytes

Analyte	Concentration in Digest	Analyte	Concentration in Digest
Pb	500 ppb	Tl	2000 ppb
Se	2000 ppb		

Tables based on a final volume of 100 mL.

APPENDIX D, PROCEDURE CHECKLIST

SW846-3050B

ICP/FAA

- [ ] 1.0-2.0g Sample
- [ ] Add Spikes
- [ ] 5 mL H_2O
- [ ] 5 mL HNO_3
- [ ] Heat 15 min
- [ ] Cool
- [ ] 5 mL HNO_3
- [ ] Heat 30 min
- [ ] Repeat (5 mL HNO_3) until no brown fumes exist
- [ ] Reduce to 5 mL or heat 2 hours
- [ ] Cool
- [ ] 2 mL H_2O
- [ ] 3 mL H_2O_2
- [ ] Heat until effervescence subsides
- [ ] Cool
- [ ] Repeat with 1 mL aliquots H_2O_2 until effervesence is minimal or 7 times
- [ ] Reduce to 5 mL or heat 2 hours
- [ ] Cool
- [ ] 10 mL HCl
- [ ] Heat 15 min
- [ ] Cool
- [ ] Final Volume 100 mL

GFAA/ICP-MS

- [ ] 1.0-2.0g Sample
- [ ] Add Spikes
- [ ] 5 mL H_2O
- [ ] 5 mL HNO_3
- [ ] Heat 15 min
- [ ] Cool
- [ ] 5 mL HNO_3
- [ ] Heat 30 min
- [ ] Repeat (5 mL HNO_3) until no brown fumes exist
- [ ] Reduce to 5 mL or heat 2 hours
- [ ] Cool
- [ ] 2 mL H_2O
- [ ] 3 mL H_2O_2
- [ ] Heat until effervescence subsides
- [ ] Cool
- [ ] Repeat with 1 mL aliquots H_2O_2 until effervesence is minimal or 7 times
- [ ] Reduce to 5 mL or heat 2 hours
- [ ] Cool
- [ ] Final Volume 100 mL

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #: LTL-7101

Title: **Operation of Jarrell-Ash Enviro 36 Simultaneous ICP**

Revision history:

Number	Date
1	01/23/96
2	01/09/97
3	2/4/98

Revised by: Katja Palmer Date: 02/05/98
Katja Palmer, Primary ICP Operator

Approved by: Harry Romberg Date: 2-5-98
Harry Romberg, QA Officer

Approved by: Karen J. Kotz Date: 2/5/98
Karen Kotz, Laboratory Director

UNCONTROLLED

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1. Introduction and Scope

1.1 Purpose

1.1.1 The purpose of this SOP is to define the operation of the Jarrell-Ash Enviro 36 (JA36) ICP and any tasks associated with the operation of the instrument. Specific QC requirements and method protocols are listed in their respective SOPs.

2. Equipment List and Standards

- ◊ Jarrell-Ash Enviro36 simultaneous ICP with autosampler
- ◊ Calibration standards
- ◊ Standard reference materials
- ◊ Coolant circulator
- ◊ Pump and nebulizer tubing
- ◊ 13 x 100 mm disposable culture tubes

2.1 Standards

2.1.1 All standards are made in deionized water acidified with 5% HCl and 1% HNO_3. Each completed standard contains 50 ppm of Scandium internal standard. Expiration dates for the standards are based on the expiration date of the purchased stock standard solution. Daily working standards are made up as needed.

2.1.2 The standards used for routine ICP operation are:

- ◊ A Blank Standard
- ◊ A High Standard
- ◊ Mid range standards(for SW846 6010 A only)
- ◊ CCB (continuing calibration blank)
- ◊ CCV(continuing calibration verification)
- ◊ ICB (Initial Calibration blank)
- ◊ ICV (Initial calibration verification)
- ◊ ICSA (interference check sample A)
- ◊ ICSAB (interference check sample B)
- ◊ CRI (low detection limit sample)

2.1.3 Additionally, every quarter an IDL standard is analyzed, on three non-consecutive days. The exact concentrations of the IDL standards are listed in appendix 2. Annually, the MDL standard is digested and analyzed as part of an MDL study. The concentration of the MDL standard used for the study is documented in the MDL study file.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances.

- Sample digests are acid solutions, use routine acid handling care.
- Concentrated metals standards should be handled with care so that none are absorbed through the skin.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Do not look directly at the torch without the polarizing shield as the UV rays emitted will cause eye damage.

3.1.4 Do not try to operate the instrument with the front door of the torch compartment open by bypassing the interlock.

3.1.5 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.6 Electrical shock - All instruments present the possibility of electrical shock The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

- Do not attempt to change the power amplifier tube as extremely high voltage may cause electrical shock. Call service engineer to perform this task.
- Do not remove any panels of the RF generator as exposure to microwaves will occur.

3.2 Waste Disposal

3.2.1 Waste is collected in the carboy under the torch compartment. Empty as necessary. Always leave about six-inches of waste in the bottom.

3.2.2 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

4. Calibration and Quality Control

4.1 Calibration Procedure

4.1.1 A SPEX multi-element standard and a Blank standard are used to calibrate the instrument. If running in the autosampler mode, the standards are included at the beginning of the autosampler table.

4.1.2 In the manual mode, select **Operation** from the main menu then select **Analysis.**

4.1.3 Enter the name of the method used or accept the default method. Press F3 for standardization.

4.1.4 Use the arrow keys to highlight the name of the standard. Aspirate the standard and press "F1" (run). Repeat until all standards have been run. Press "F9" twice to return to the analysis menu.

4.2 Quality Control and Limit Check Tables

Note: These tables are method specific (SW846, 200.7 and CLP) and must be applied appropriately.

4.2.1 Quality control check tables are used with QC samples. They contain the true values of the ICVs, the acceptable range of the results according to the method being run, and the units of comparison: percent or absolute. QC Check tables are only used when a sample is defined as a QC sample.

4.2.2 Limit check tables are used with analytical samples and with blank samples (i.e. ICBs and CCBs). The control limits for blanks are dependent on the method being run. They are generally defined as being the absolute value of the result. They should not exceed the reporting limit. For analytical samples their upper range is set as the linear range of the instrument or the level of the high standard, depending on the specifications of the method being run. The lower limit is set at the negative reporting limit, again method specific.

4.2.3 Method information and the QC and Limit tables for each method can be found in **Appendix 3.**

5. Operation procedures

5.1 Startup

- The argon tanks, located in the warehouse, are connected to a delivery manifold that will allow a continuous flow of argon as long as there is 90 psi available in a tank. The line-in pressure regulator is located behind the instrument and is to be adjusted to 50 psi.

- Check pump tubing to see if it is flat or crimped. Change if necessary. Check all connections to see if any blockage exists and if clogs are found, remove them by disconnecting the tubing and flushing with DIW or by using a cleaning wire.

- Turn on control and line breakers on the RF generator.

- Turn on the computer power strip and the power strip attached to the autosampler cart.

- Turn on the torch, auxiliary, and sample argon toggles on the front of the instrument. Let the argon purge through the system for about 3 minutes.

- Settings: torch=18
  aux=0.5
  sample=0.65.

- At the computer select OPERATION, ANALYSIS, accept the default method, and at the command line type **iara** <ENTER>.

- Stretch the rinsate pump tubing into place, set the pressure plate, and turn on the peristaltic pump.

- Prior to igniting the torch aspirate rinse water into the nebulizer. Observe the spray chamber to ensure the aspirated solution is being nebulized.

- Turn off the sample argon toggle to halt gas flow into the nebulizer.

- Press the red RF ON button, then turn the power knob until the forward power reads about 0.5 on the meter.

- Press the ignite button to light the torch. If the torch does not light the first time try again. If it still does not light, adjust the forward power slightly higher until the torch lights while pressing the ignite button. The torch is lit when white streams appear at the top of the torch.

- Slowly increase power until a plasma forms (white "flame"). This will be accompanied by "popping" sounds as the plasma begins to form.

- If the torch appears yellow-orange during this process, depress the blue RF OFF button immediately and turn the power knob back to the off position. This yellow-orange color means that the torch is overheating. See the manufacturers manual, page 14, for corrective action.

- Adjust the forward power to 1.1 KW.

- Switch the automatic power toggle from manual to automatic.

- Slowly turn the power knob fully clockwise.

5.2 Automatic Profiling

- Select OPERATION from the main menu.

- Select ANALYSIS from the menu.

- Accept the default method.

- Set the 5 ppm Mn profiling solution on the autosampler tray at rack #2 position 75 (the white dotted circle). At the command line of the software type **iasrn2srt70ma75** <ENTER>. Translation: Initialize Autosampler, Set Rack Number 2, Set Rack Type 70, Move Autosampler to position #75.

- Select F5 (Profile) from the function keys.

- Select F3 (Automatic) from the function keys.

- Type in a 40 second flush time.

- Press F1 (Run) from the function keys.

- If the peak is between 0.1 and -0.1, the instrument is profiled. If the peak is outside of this range a manual profile is required.

5.3 Manual Profiling

- With the Mn standard still being aspirated, select F1 (manual profile) from the Profile menu.
- Moving the micrometer screw, maximize the reading on the profile meter.
- Move the micrometer screw clockwise until the profile meter reads less than 70% of the maximum. Record the value of the micrometer screw.
- Continue moving the micrometer screw counterclockwise, past the maximum reading on the profile meter, until the profile meter once again reads less than 70% of the maximum. Record the value of the micrometer screw.
- Determine the average of the two values.
- Set the micrometer at the average value by moving the screw in a counterclockwise direction.
- Repeat the auto-profile to check the peak position.

5.4 Analytical Operation

5.4.1 All analytical solutions aspirated into the ICP must contain 50 ppm Sc. 50 µL of 10000 ppm scandium is added to a 10 ml aliquot of sample. If samples are to be run manually aspirate right out of the tube. If they are to be included in an autosampler run, pour the sample into a culture tube and load the tube into the appropriate spot in the autosampler tray.

5.4.2 If samples are to be run in the autosampler mode it is necessary to set up the autosampler table. From the menu choose **Autosampler setup.** Select the table name. Press "F1"(edit autosampler table). Type in the sequence of samples.

5.4.3 To analyze samples in the manual mode it is necessary to be in the **Analysis** menu. After the instrument has been calibrated, press "F2". Fill in the requested information. Aspirate the ICV. Press "F1"(run). For the ICB, use "F4"(Blank sample). For analytical samples use "F1"(analyze). Repeat for additional reference samples and then for "real" samples.

5.4.4 To analyze samples in the autosampler mode it is also necessary to be in the **Analysis** menu. Enter the desired method or accept the default Method. Calibration will be done by the autosampler table. Press "F9"(Autosampler). Type in the name of the autosampler table and press the "ENTER" key. Verify that the standards and the samples are in the correct positions. Press " F1"(start).

5.4.5 For more details on creating Tables and Methods refer to the Operators Manual for the ICP.

5.5 Shutdown Procedure

5.5.1 Turn the power knob on the RF generator off (left) and press the red reset button when the alarm sounds. Press the blue RF OFF button. Then flip the toggle switch for the automatic power control to the manual position.

5.5.2 The control and line breaker switches only need to be turned off for weekends or if the instrument is not going to be used the next day. This should be done after the RF power has been off for at least 5 minutes.

5.5.3 Turn off the power strip on the autosampler cart.

5.5.4 Release the pressure plates on the peristaltic pump and unhook the pump tubing.

5.5.5 Turn off the torch, auxiliary, and sample argon toggles on the front of the instrument.

5.5.6 If the computer will not be used, turn off the master switch on the computer power strip.

6. Reports

6.1 Results

6.1.1 All Results are organized into Data packets. The format of each packet is dependent on the method and protocol required for that specific job. Details for method specific reports can be found in the method SOP.

6.2 Quality Control Reports

6.2.1 All results for quality control tests are entered into the lab data base using the Quality Control database QC_DB. Printouts of all data entered must be included in the data

packet. The routine minimum is a method blank report, and an MS/MSD or MS/duplicate report. Many analyses will also require an SRM (LCSS), blank spike (LCSW) or other report. The recovery values for Ag,Al,Cr,Cd and B in the LCSS and LCSW are plotted on control charts.

6.2.2 Method specific QC requirements are listed in the Method SOP.

7. Quarterly and Yearly Procedures

7.1 Instrument Detection Limits (IDLs)

7.1.1 For complete details on performing IDL studies refer to Laucks SOP LTL-1011. In brief, IDLs for each analyte are determined quarterly by analyzing a "sample" seven consecutive times. This is done on three non-consecutive days. Calculate the standard deviation of the seven results on a given day. Add the standard deviations from the three days and the result is the IDL. The IDL solution is at a concentration of 3-5X the expected IDL. The IDL standard is not digested. The exact concentrations for the IDL standard are listed in **Appendix 2** of the SOP.

7.2 Method Detection Limits (MDLs)

7.2.1 For complete details on performing IDL studies refer to Laucks SOP LTL-1011 . In brief, MDLs for each analyte are determined yearly by analyzing seven replicates of a digested solution. MDLs are run according to the Laucks SOP on MDL determinations using the appropriate method. The MDL solution concentration is documented in the MDL study file.

7.3 Linear Range

7.3.1 CLP and EPA 200.7 - Linear ranges for each analyte are determined by analyzing a high concentration "sample". The analytically determined concentration must be within 5% of the true value. The true value is the upper limit of the ICP linear range. Linear range must be verified quarterly. A list of the ICP linear ranges can be found in **Appendix 2** of this document.

7.3.2 SW846 6010B - The upper limit of the linear dynamic range must be established by running a multi-point calibration using 4 standards and then running an upper range standard. The upper range limit should be an observed signal with no more than a 10%

variation from the true value of the upper range standard. Linear range must be checked every six months.

7.4 Interelement Correction Factors (IECs)

7.4.1 Interelement correction factors are determined by analyzing single element, high concentration samples. The apparent concentration of an analyte divided by the concentration of an interfering analyte run at 100 ppm, gives the required correction for that analyte/interfering element combination. This must be verified and updated for all analytes and all interfering elements every six months.

Appendix 1

Concentration of analytes in standard solutions in mg/L for CLP/200.7 and SW846 6010B

ELEMENT	ICAL STD	ICV	CCV	ICSA	ICSAB	CRI
Ag	1.0	0.6	0.5	-	1	0.02
Al	20.	12	10	500	500	-
As	1.0	2.6	2.5	-	1	0.02
Ba	20.	12	10	-	0.5	-
Be	0.5	0.3	0.25	-	0.5	0.01
Ca	50.	300	25	500	500	-
Cd	0.5	0.3	0.25	-	1	0.01
Co	5.0	3	2.5	-	0.5	0.10
Cr	1.0	0.6	0.5	-	0.5	0.02
Cu	2.5	1.5	1.25	200	0.5	0.05
Fe	10.	6	5	-	200	-
Hg	2.0	2	1	-	-	-
K	50.	300	25	500	-	-
Mg	50.	300	25	-	500	-
Mn	1.5	0.9	0.75	-	0.5	0.03
Na	50.	300	25	-	-	-
Ni	4.0	2.4	2	-	1	0.08
Pb	0.5	2.3	1	-	1	0.056
Sb	6.0	3.6	3	-	-	0.12
Se	0.5	2.3	2.5	-	1	0.01
Tl	1.0	0.6	5	-	1	0.02
V	5.0	3	2.5	-	0.5	0.10
Zn	2.0	1.2	1	-	1	0.04
Mo	5.0	10	2.5	-	-	-
B	5.0	10	2.5	-	-	-

* ICV and CCV have different stock solutions

Appendix 1. cont.

Concentration of analytes for SW846 6010A calibration standards in mg/l

ELEMENT	Std 1 (low std)	Std 2 (mid std)	Std 3 (mid-hi std)	Std 4 (high std)
Ag	0.02	0.2	1.0	2.0
Al	1.0	10.	50.	100.
As	0.05	0.5	2.5	5.0
Ba	0.2	1.0	5.0	10.
Be	0.01	0.1	0.5	1.0
Ca	4.0	40	200.	400.
Cd	0.02	0.2	1.0	2.0
Co	0.05	0.5	2.5	5.0
Cr	0.05	0.5	2.5	5.0
Cu	0.05	5.0	25.	50.
Fe	2.0	20.	100.	200
Hg	0.05	0.5	2.5	5.0
K	3.0	30.	150.	300
Mg	2.0	20.	100.	200.
Mn	0.1	1.0	5.0	10.
Na	2.5	25	125.	250.
Ni	0.1	1.0	5.0	10.
Pb	0.1	5.0	25.	50.
Sb	0.05	0.5	2.5	5.0
Se	0.05	0.5	2.5	5.0
Tl	0.1	1.0	5.0	10.
V	0.1	1.0	5.0	10.
Zn	0.1	5.0	25.	50
Mo	0.2	1.0	5.0	10.

* SW846 H.std=ICV

Appendix 2

IDL solutions and linear range for CLP/200.7

ELEMENT	IDL solution T.V. (mg/L)	linear range (mg/L)
Ag	0.01	200.
Al	0.05	600.
As	0.04	300.
Ba	0.01	100
Be	0.002	10.
Ca	0.05	600
Cd	0.005	100
Co	0.01	200
Cr	0.02	200
Cu	0.01	200
Fe	0.05	600
Hg	0.04	-
K	0.45	1000
Mg	0.05	600
Mn	0.02	100
Na	0.05	600
Ni	0.01	200
Pb	0.04	200
Sb	0.02	200
Se	0.05	200
Tl	0.05	10
V	0.04	200
Zn	0.002	200
Mo	0.01	-
B	0.2	-

Appendix 3

Method information, QC and limit check tables

Method: LAUCKIEC

Applicable to CLP/200.7

METHOD INFORMATION

Sample Introduction Device: Normal
Calibration Mode: Concentration

Default Setup:

Number of Repeats : 4		Auto-store Analysis Data?	Yes
Flush Time (sec) :60.0		Auto-store Stdzn Data?	No
Auto-Increment Sample Names?No		Store Individual Repeats?	Yes
		Auto-print Analysis Data?	Yes
		Auto-print Stdzn Report?	None
		Condensed Print Format?	No

Default File Names:

Analysis Data File	: MIKEDAT	Autosampler Table	: AUTO
		Sample Limits Table	: LINCHK
Calibration Data File	: DEFAULT	Blank Limits Table	: MGLBLK
Calibration Stds Table	: DEFAULT	QC Check Table	SPEXCCVM

Limit Check Table LINCHK
limit values in ppm

ELEMENT	High limit	Low limit
Ag*	200.	-.01
Al*	600.	-.2
As*	300.	-.3
Ba*	200.	-.1
Be*	100.	-.005
Ca*	600.	-1.
Cd	100.	-.005
Co	200.	-.05
Cr	200.	-.01
Cu	200.	-.025
Fe	600.	-.1
Mg	600.	-1.
Mn	100.	-.015
Na	600.	-1
Ni	200.	-.04
Pb	200.	-.1
Sb	200.	-.06
Se	200.	-.3
Tl	10.	-.5
V	200.	-.05
Zn	200.	-.02
K	1000	-1
B	100.	-.2
Mo	100.	-.01

Limit Check Table MGLBLK
limit values in ppm

Element	High limit	Low limit
Ag*	.01	-.01
Al*	.2	-.2
As*	.2	-.2
Ba*	.2	-.2
Be*	.005	-.005
Ca*	1.	-1.
Cd*	.005	-005
Co*	.05	-.05
Cr*	.01	-.01
Cu*	.025	-.025
Fe*	.1	-.1
Mg*	1.	-1.
Mn*	.015	-.015
Na*	1.	-1.
Ni*	.04	-.04
Pb*	.05	-.05
Sb*	.06	-.06
Se*	.2	-.2
Tl*	.5	-.5
V*	.05	-.05
Zn*	.02	-.02
K*	1.	-1.

QC Check Table SPEXICVM and BMOICVM
limit values in ppm

Element	Value	% Range
Ag*	.6	10
Al*	12.	10
As*	2.6	10
Ba*	12.	10
Be*	.3	10
Ca*	300.	10
Cd*	.3	10
Co*	3	10
Cr*	.6	10
Cu*	1.5	10
Fe*	6.	10
Mg*	300.	10
Mn*	.9	10
Ni*	2.4	10
Pb*	2.3	10
Sb*	3.6	10
Se*	2.3	10
Tl*	.6	10
V*	3.	10
Zn*	1.2	10
K*	300.	10
B	10	10
Mo	10	10

QC Check Table SPEXCCVM
limit values in ppm

Element	Value	% Range
Ag*	.5	10
Al*	10	10
As*	2.5	10
Ba*	10	10
Be*	.25	10
Ca*	25	10
Cd*	.25	10
Co*	2.5	10
Cr*	.5	10
Cu*	1.25	10
Fe*	5	10
Mg*	25	10
Mn*	.75	10
Na*	25	10
Ni*	2	10
Pb*	1	10
Sb*	3	10
Se*	2.5	10
Tl*	5	10
V*	2.5	10
Zn*	1	10
K*	25	10
Hg*	1	10
B*	2.5	10
Mo*	2.5	10

* QC Check Table SPEXCCVM valid for CCVs in all current Methods

Method: SW846

Applicable to SW846 Soils

METHOD INFORMATION

Sample Introduction Device: Normal
Calibration Mode: Concentration

Default Setup:

Number of Repeats : 4
Flush Time (sec) : 60.0
Auto-Increment Sample Names? No

Auto-store Analysis Data? Yes
Auto-store Stdzn Data? No
Store Individual Repeats? Yes
Auto-print Analysis Data? Yes
Auto-print Stdzn Report : None
Condensed Print Format? No

Default File Names:

Analysis Data File : MIKEDAT
Calibration Data File : DEFAULT
Calibration Stds Table: DEFAULT

Autosampler Table : AUTO
Sample Limits Table : HCALSTD
Blank Limits Table : MDL2X
QC Check Table : SPEXCCVM

Limit Check Table HICALSTD
limit values in ppm

Element	High limit	Low Limit
Ag*	2	-.0055
Al*	100	-.221
As*	5	-.057
Ba*	10	-.038
Be*	1	-.003
Ca*	400	-1.008
Cd*	2	-0063
Co*	5	-.0129
Cr*	5	-.0199
Cu*	50	-.0177
Fe*	200	-.4988
Mg*	200	-.5198
Mn*	10	-.0247
Na*	250	-.5528
Ni*	10	-.0365
Pb*	50	-.059
Sb*	5	-.033
Se*	5	-.1005
Tl*	10	-.0668
V*	10	-.0255
Zn*	50	-.036
K*	300	-.5472
MO*	10	-0783

* HCALSTD Table low limit based on 2X current soil MDL and subject to change annually

Limit Check Table MDL2X
limit values in ppm

Element	High Limit	Low Limit
Ag*	.0055	-.0055
Al*	.221	-.221
As*	.057	-.057
Ba*	.038	-.038
Be*	.003	-.003
Ca*	1.008	-1.008
Cd*	.0063	-.0063
Co*	.0129	-.0129
Cr	.0199	-.0199
Cu	.0177	-.0177
Fe*	.4988	-.4988
Mg*	.5198	-.5198
Mn*	.0247	-.0247
Na*	.5528	-.5528
Ni*	.0365	-.0365
Pb*	.059	-.059
Sb*	.033	-.033
Se*	.1005	-.1005
Tl*	.0668	-.0668
V*	.0255	-.0255
Zn*	.036	-.036
K*	.5472	-.5472
Mo*	.0783	-.0783

* Blank Limits based on 2X soil MDL and therefore subject to annual variations

QC Check Table HSTDICVM
limit values in ppm

Element	Value	% Range
Ag*	2	5
As*	5	5
Ba*	10	5
Ca*	400	5
Be*	1	5
Al*	100	5
Cd*	2	5
Co*	5	5
Cr*	5	5
Cu*	50	5
Fe*	200	5
Hg*	5	5
K*	300	5
Mg*	200	5
Mn*	10	5
Na*	250	5
Ni*	10	5
Pb*	50	5
Sb*	5	5
Se*	5	5
Tl*	10	5
V	10	5
Zn*	50	5
Mo*	10	5

Method: SW846W

Applicable to SW846 Waters

METHOD INFORMATION

Sample Introduction Device: Normal
Calibration Mode: Concentration

Default Setup:

Number of Repeats 4
Flush Time (sec) 60.0
Auto-Increment Sample Names? No

Auto-store Analysis Data? Yes
Auto-store Stdzn Data? No
Store Individual Repeats? Yes
Auto-print Analysis Data? Yes
Auto-print Stdzn Report : None
Condensed Print Format? No

Default File Names:

Analysis Data File: MIKEDAT
Calibration Data File: DEFAULT
Calibration Stds Table: DEFAULT
Calibration Stds Table: DEFAULT

Autosampler Table AUTO
Sample Limits Table HCALSTDW
Blank Limits Table WMDL2X
QC Check Table SPEXCCVM

Limit Check Table HCALSTDW
limit values in ppm

Element	High Limit	Low Limit
Ag*	2	-.0082
Al*	100	-.1864
As*	5	-.0528
Ba*	10	-.0119
Be*	1	-.001
Ca*	400	-.346
Cd*	2	-.0213
Co*	5	-.0057
Cr *	5	-.0157
Cu*	50	-.0051
Fe*	200	-.163
Mg*	200	-.253
Mn*	10	-.008
Na*	250	-.1975
Ni*	10	-.0086
Pb*	50	-.04
Sb*	5	-.0154
Se*	5	-.0698
Tl	10	-.071
V*	10	-.0051
Zn*	50	-.0147
K*	300	-.288
Mo*	10	-.0233

* Low sample limit bases on 2X Water MDL. Subject to change annually.

Limit Check Table WMDL2X
limit values in ppm

Element	High Limit	Low Limit
Ag*	.0082	-.0082
Al*	.1864	-.1864
As*	.0528	-.0528
Ba*	.0119	-.0119
Be*	.0009	-.0009
Ca*	.346	-.346
Cd*	.0213	-.0213
Co*	.0057	-.0057
Cr*	.0157	-.0157
Cu*	.0051	.0051
Fe*	.163	-.163
Mg*	.253	-.253
Mn*	.008	-.008
Na*	.1975	-.1975
Ni*	.0086	.0086
Pb*	.04	-.04
Sb*	.0154	-.0154
Se*	.0698	-.0698
Tl*	.071	-.071
V*	.0051	-.0051
Zn*	.0147	-.0147
K*	.288	-.288
Mo*	.0233	-.0233

* Blank limits bases on current Water MDLs. Subject to annual variation.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-7105

Title: Method Protocols for the Analysis of Metals by ICP Using SW 846 6010B

Revision history:

Number	Date
0	1/29/98
1	03/24/00

Controlled Document

No. 20 Assigned to: Tetra

Revised by: _____ Date: 03/24/2000

Paul Swift, Metal Supervisor

Approved by: _____ Date: 3-24-2000

Harry Romberg, Quality Assurance Officer

Approved by: _____ Date: 03-24-2000

Kathy Kreps, Laboratory Director

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Introduction and Scope

1.1 Scope

This method is to be used as a supplement to the instrumental SOP in order to follow the method requirements of SW 846 6010B for ICP analysis. Operating parameters are to be followed in the individual instrument SOP.

The analyst should become familiar with SW 846 protocols prior to using this SOP.

This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Sample Collection, Sample Storage, Holding Times

Samples are to be collected in either glass or plastic containers. Water samples are to be preserved to a pH < 2 using nitric acid. A one liter sample bottle is sufficient volume for analysis. Soil samples do not require preservation but need to be stored at 4° C. At least 200 grams of sample should be collected. The holding time for ICP metals is 6 months. See Appendix III for Sample Handling and Preservation Table.

1.3 Definition of Terms

This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

ICV - Initial Calibration verification - This is a standard run immediately following the initial calibration. The ICV is made from an independent source. Agreement within 10% and a relative standard deviation less than 5% RSD from replicate (minimum of two) integrations, is required.

ICB - Initial calibration blank - An instrument blank is made up in the same way as calibration standards, without target analytes.

CCV - Continuing calibration verification. - This is a standard analyzed after every 10 samples during the analysis sequence to determine whether the instrument or system has remained in calibration. Agreement within 10% and less than 5% RSD from replicate (minimum of two) integrations, is required.

CCB - Continuing Calibration Blank - This is a blank that is used to determine if there is carry-over between sample injections. A CCB succeeds every CCV, every 10 samples.

CRDL - Contract Required Detection Limit - The minimum level of detection at ±20% analyte recovery. This limit represents the analyte concentrations below which data must be evaluated and qualified as estimated concentrations. The commercial CRDL solution may be used as a check standard, but must be fortified with As, Pb, and Se to a final concentration before analysis of 10ug/L.

DIW - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

IEC - Interelement Correction Factors - IECs are experimentally-determined constants used by the calibration modelling software in estimating the extent of intereference caused by IEC elements on the other analyzed elements. This list is to include the nine interferents listed in SW846 Method 6010B - Al, Ca, Cr, Cu, Fe, Mg, Mn, Tl, and V.

ICSA - Interference Check Solution A - This solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors.

ICSAB - Interference Check Solution AB - This solution is prepared by spiking the ICSA with known quantities of analyte. Adequate recovery of the analytes within this interfering matrix indicates proper application of the correction factors.

IDL - Instrument detection limit - The lowest concentration of a target analyte that is detectable. The IDL is three times the average standard deviation of seven replicates at 2 to 5 times the estimated IDL over three non consecutive days. Used as a starting point for selecting MDL study spiking levels. IDL should be determined quarterly.

Method Blank Sample / Preparation Blanks Sample- A sample containing only reagent and representative matrix (DIW or blank solid material, as appropriate). This sample is to be carried through the entire preparation procedure and analyzed as a regular sample. The level of analytes in this sample must not exceed one-half the concentrations requested as reporting limits for the project, or twice the MDL, whichever is lower. Corrective action will be either qualification of data associated with that blank sample or repreparation/reanalysis of the associated samples.

MS - Matrix spike. The matrix spike sample is to be prepared such that the amounts of analyte added are near the action levels of concern for the project, but above 20x the MDLs. Preparation of the matrix spike sample is described in the appropriate SOP.

MDL - Method detection limit - The lowest concentration which will yield a positive result that is greater than zero at a known level of confidence. The MDL is preparation specific and empirically determined by Laucks.

LCS - Laboratory Control Sample - This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This sample is used to demonstrate that the analytical system is in control. It may be considered to be a blank spike for most inorganic analyses and is preferred over artificially spiking blank materials.

Post digestion spike - The sample selected for QC analysis will be post-spiked and analyzed in the event that the matrix spike sample exceeds recovery criteria. The final spike level should be identical to the predigestion spike, near the action levels of concern for the project but above 20x the MDL.

QC period - Quality control period - An analysis sequence initiated by the analysis of one or more standards, followed by samples, and terminated with a standard and blank analysis.

RSD or %RSD - Relative standard deviation or percent relative standard deviation - The ratio of the standard deviation of a set of values to the mean of the set of values. A measure of the similarity of the values one to another.

Sequence - A set of sample digests and standard solutions introduced into an instrument in a chronologically continuous group.

2. Equipment List and Standards

2.1 Instrumentation:

Thermo Jarrell Ash Enviro 36 simultaneous ICP, Thermo Jerrall Ash ICAP 61E Trace Analyzer or equivalent.

2.2 Standards
SW 846 Method 6010B requires the use of one standard and a blank. See the instrument SOP for standards and their preparation.

3. Safety precautions and Waste Disposal

See instrument SOP for detailed safety precautions and waste disposal.

Safety

All standards, samples and sample solutions should be handled as if they are hazardous substances.

Refer to the instrument manufacturer's manual for routine instrument precautions.

Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

Electrical shock - All instruments present the possibility of electrical shock The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

Caution should be used when handling acidic digestates.

3.1 Waste Disposal

Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on waste segregation and disposal.

4. Calibration and Quality Control

4.1 Method Detection Limit Study

Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in the Laucks SOP on performing MDL studies. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration approximately 3 to 5 times the estimated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL.

4.2 Linear range study

The upper limit of the linear dynamic range must be established by running a multi-point calibration using 4 standards and then running an upper range standard. The upper range

limit should be an observed signal with no more than a 10% variation from the true value of the upper range standard. All samples with elements exceeding the level of the upper range standard must be diluted.

4.3 Initial Calibration and Preliminary Calibration Check Standards

Analyze standard solutions using a minimum of a calibration blank and one standard. The calibration curve must be verified by running an Initial Calibration Standard (ICV) and obtaining agreement within 10% of the expected concentration and a 5% RSD for replicate integrations.

One check standard at the CRDL is to be analyzed, and the recovery criteria shall be ±20%.

One check standard at or below the linear range for each analyte may be analyzed in order to confirm the linearity of the calibration curve between the single-point high standard and the estimated linear range maxima. Recovery of 90-110% allows the use of the calibration curve in this region to quantify sample results.

Criteria and Corrective Action:

Calibration - Since a linear regression is not possible when using a two point calibration on the Enviro 36, the standard curve is validated by evaluating the ICV and the subsequent CCVs. If the corresponding control limits for the ICV and CCV are exceeded, then the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable ICV, CCV must be reanalyzed.

Linear range standard - If this standard is not included in the analysis then any data acquired with concentration values above the high standard but within the linear range of the instrument must be qualified as estimated quantities. Preferably, the samples would be diluted and reanalyzed

CRDL - If the stated criterion cannot be met then the reporting limit will be adjusted such that this analysis will be in control. This may involve adjusting the CRDL concentration for individual analytes which failed to meet acceptance followed by reanalysis.

4.4 Initial Calibration Standard ICV:

Immediately after the calibration curve, an ICV is analyzed.

The calculated concentration of the standard must be within 10% of the expected value and the RSD must be less than 5% for replicate integrations.

Corrective Action:

If the ICV criteria are not met, no samples can be analyzed. Perform system maintenance and re-check the ICV. If the criteria still cannot be met, the system must be recalibrated.

4.5 Initial Calibration Blank

After the analysis of the high standard, an instrument blank (ICB) is analyzed. The levels of target analytes in the ICB should not exceed three times the instrument detection limit.

Corrective Action:

If the ICB analyte levels exceed 3 times the IDL, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, the system is out of control. The source of contamination must be identified and corrected before proceeding with the analysis. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.

4.6 Continuing Calibration Verification (CCV) and Blank (CCB)

A continuing calibration verification standard is analyzed after every 10 samples. Immediately following the CCV, a blank solution is analyzed. In addition, this standard and blank must be the last samples analyzed in the run. The CCV must also be prepared from an independent source.

The CCV must fall within ± 10% of the true value and the RSD must be less than 5% for replicate integrations.

The levels of target analytes in the CCB should not exceed 3 times the IDL.

Corrective action:

If CCV limits are exceeded, check calculations or perform instrument maintenance. Recalibrate and reanalyze. No sample results may be reported that are not bracketed by a successful calibration and a CCV/CCB which is in control or by preceding and following CCV/CCBs which are within limits.

If the CCB analyte levels exceed 3 times the IDL, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background

mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within ten percent of the action limit, analyses need not be rerun and recalibration need not be preformed before continuation of the run.

4.7 Interference Check Solutions A (ICSA) and AB (ICSAB)

(ICSA):

At the beginning and at the end of each run, an interference check solution A is analyzed. This solution contains interefering elements only. All other elements are not present in the solution. All elements not present should show a recovery of zero, or ± the CRDL.

Corrective Action:
If the analytes do not recover within the specified control limits, then the system is out of control. The problem needs to be identified and corrected prior to beginning another run.

(ICSAB):

At the beginning and end of each analytical sequence an ICSAB must be analyzed. Analytes must recover between 80-120%.

Corrective Action:

If the analytes do not recover within the specified control limits, then the system is out of control. The problem needs to be identified and corrected prior to beginning another analysis.

4.8 Method Blanks

Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time or at least one blank every 20 samples, which ever is more frequent. Any analyte response above the MDL is reported. For a method blank to be acceptable for use with the accompanying samples, the concentration of the blank of any analyte of concern should not be higher than the highest of either:

(1) One-half of the reporting limit, which is approximately twice the value of the MDL, or
(2) Five percent of the regulatory limit for that analyte, or
(3) Five percent of the measured concentration in the sample.

Corrective Action:

Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if an analyte was detected in the blank but not in any of the associated samples then sample group may not require re-analysis. In any case, if re-preparation and re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Control Officer. It is the laboratory's responsibility to ensure that method interference caused by contaminants in acids, solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the analytical run be minimized. In the extreme case of chronic contamination, blanks may have to be analyzed from each stage of the sample processing to determine the contamination source so it can be eliminated. In all cases where blank contamination exceeds the control limit, a narrative comment must be made which documents the corrective actions taken.

4.9 Laboratory Control Sample

The LCS is made from an independent source of the same matrix (soil or water) and is carried through the entire digestion procedure. The LCSW is to be spiked at a level near the action levels of concern for the project but above 20x the MDL. The SDG Routing Form will indicate appropriate spike level. An LCS is performed with each digestion batch. At a minimum, LCSW(water) control limit are 80% to 120%. Control limits for the LCSW will be empirically determined and must be within the method specified control limit noted aboved.

LCSS (soil) control limits are supplied by the manufacturer. LCSS control limits are not derived by the laboratory due to the small number of data points available from each lot of certified material.

Corrective Action

If the LCS is not within the required control limits but the matrix spike is in control, corrective action may not be required unless otherwise specified. If both LCS and matrix spikes exceed limits, particularly if the recoveries are low <u>or</u> there are reportable quantities of the affected target analytes, then a redigestion will occur for the affected analytes. Other extenuating circumstances may exist that allow for exceptions without redigestion and reanalysis but they must first be approved by QA.

4.10 Matrix Spike

Unless specific samples are specified for use as matrix Spike Samples, a sample is chosen at random from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to preparation. Spike samples will be identified on the SDG Routing Forms as

required. The analyst should attempt to avoid selecting samples which are identified by the client as blanks.

The matrix spike sample is to be prepared such that the amounts of analyte added are near the action levels of concern for the project, but above 20x the MDLs. Preparation of the matrix spike sample is described in the appropriate SOP.

As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may also avoid selecting the most difficult sample of the batch for spiking. It is not always required that a matrix spike analysis be performed with each preparation/analysis-batch, however, the minimum frequency for MS analysis is 1 each per 20 samples per matrix. This will be best accomplished by running one with every batch for many analyses. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$recovery,\% = \frac{(SS - S)}{SA} * 100$$

where:

SS = concentration in spiked sample
S = native concentration in unspiked sample
SA = spike added, the amount of spiking material actually added calculated on the sample basis.

For ICP, control limits for spike recoveries will be 75-125% unless otherwise specified in the project specific QAPP. In-house control limits are based on historical performance. The recovery criteria are detailed in the QC Database QC_DB and will change from time to time.

Corrective Action:

Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action will first involve recalculation, followed by possible re-preparation, and/or reanalysis. This process should also look at the recovery of matrix spiking compounds from the SRM and/or blank spike analysis.

In some cases a Post Digestion Spike is required when matrix interference is suspected. The sample selected for QC analysis will be post-spiked and analyzed in the event that the matrix spike sample exceeds recovery criteria. The final spike level should be identical to the predigestion spike, near the action levels of concern for the project but above 20x the MDL. The same 75-125% recovery criteria exist for this spike as for the matrix spike or a matrix effect is expected. In all cases a narrative explanation of the condition is required to detail

the corrective actions taken. Data reported in validatable packages will be flagged with an "N" indicating the out-of-control event..

4.11 Matrix Spike Duplicate/Sample Duplicate

Method QC consists of MS/MSD. A duplicate maybe be performed instead of a MSD. Other types of QC can performed at the client's request.

Criteria

At least one matrix spike duplicate sample per 20 samples per matrix is required when matrix spikes are being performed. RPD values are calculated in a manner similar to MS/MSD RPDs:

$$RPD = \frac{|SS - SSD|}{(SS + SSD)/2} * 100$$

where:
SS = concentration in spiked sample
SSD = concentration in matrix spiked duplicate sample

For sample concentractions greater than ten times the IDL, control limits for RPD of duplicates will be ±20% unless otherwise specified in the project specific QAPP. For sample concentrations less than ten times the IDL, control limits for the difference will be ± the reporting limit. In-house control limits are based on historical performance. The RPD control limits are detailed in the current QC Database QC_DB and will change from time to time.

Corrective Action:

If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer. In a validatable package, data associated with an out-of-control RPD will be flagged with an "*".

4.12 Serial Dilution

A five-fold dilution is performed on the QC sample in each analytical batch. The difference between the initial value and the serial dilution should agree within 10%. If the difference is greater than 10% on analytes that exhibit a level 50 times greater than the MDL, then results for those analytes will be flagged with an "E".

Corrective Action:

No corrective action is necessary other than appropriately flagging the data.

5. Operation procedures

- Calibrate the instrument with a blank and one standard.
- Immediately following the calibration, analyze the ICV followed by an ICB. Concentration values obtained for the ICV should not deviate from the actual values by more than 10% and less than 5% RSD for replicate integrations.
- Analyze both the CRDL standard and the linear range standard. The CRDL recoveries should not exceed ±20% and the linear range standard should not deviate from the actual values by more than 10% and less than 5% RSD for replicate integrations.
- Flush the system with the calibration blank solution for at least 1 minute before the analysis of each sample.
- Analyze a CCV and CCB every 10 samples. The CCV must agree within 10% of its expected value and less than 5% RSD for replicate integrations. The results of the calibration blanks are to be within 3 times the IDL. If not, repeat the analysis two or more times and average the results. If the average is not within 3 times the IDL, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

5.1 Analysis Sequence

See Appendix IV for Analytical Sequence

5.2 Instrumental Conditions

See instrument SOP for operating procedures.

5.3 Analytical Operation

See instrument SOP for operating procedures.

6. Reports

6.1 Data Packet Organization

- See the SOP metals validation for a check list detailing data packet organization
- If requested, all analysis performed under SW 846 guidelines can be reported via CLP SOW 3/90 forms. These forms provide all relevant QC information.
- Data packages will be produced via Enviroforms. Analyte levels that are less than the MDL will be reported as the SDL followed by a "U". Analyte levels that fall between the MDL and the reporting limit will be flagged with a "B". Analyte levels greater than or equal to the reporting limit PQL will be reported without a flag.

CODE	Definition	
U	The analyte of interest was not detected, to the limit of detection indicated.	❁◆
B	The analyte of interest was detected between the MDL and the reporting limit.	❁
N	The spike recovery exceeded the control limits.	❁
*	The duplicates exceeded the RPD control limit or their difference exceeded the reporting limit.	❁
E	The Serial Dilution did not agree within 10%.	❁
S	The analyte concentration was determined by MSA.	❁

◆ Used in all reports.
❁ Used in data validatable packages.

6.2 Control Chart(s)

The recovery values for ICP analytes Al, B, Cd, Cr, and Ag in the LCS are plotted on control charts. Other analytes may be added at the discretion of QA without immediate revision of this SOP.

6.3 References:

Test Methods for Evaluating Solid Waste, SW-846, Method 6010B, Revision 2, December 1996

Appendix I

QC Summary Table

Laucks Testing Laboratories

Method 6010B QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentatio
Initial Calibration	One standard and a Blank	One standard and a Blank	Beginning of each run.		In raw data.
Initial Calibration Verification	±10% of nominal value. Made from an independant source.	±10% of nominal value. Made from an independant source.	Beginning of each run immediately following ICAL.	Recalibration required.	Form 2A or in raw data.
Continuing Calibration Verification	±10% and RSD < 5% for replicate integrations.	±10% and RSD < 5% for replicate integrations.	Every 10 samples. Mid-range	Recalibrate and rerun affected samples.	Form 2A or in raw data.
Instrument Blank	±3 sigma of average.	< 1/2 reporting limit	Every 10 samples.	Recalibrate and rerun affected samples.	Form 3 or in raw data.
Method Blank	<MDL or <5% of the concentration of any sample or <5% of the regulatory limit (whichever is highest).	< one-half the reporting limit or <5% of the regulatory limit or <5% of the sample conc (whichever is highest).	One/batch	Flag data per QCO or redigest samples	Form 3, in raw data, or database report
Laboratory Control Sample		LCSW: 80%-120% LCSS: Manufacturer Specs.	One/batch	Redigest samples	Form 7, in raw data, or database report
Matrix Spike Recovery	75-125% or within documented historical limits	75-125% or current QC database criteria.	5% or per batch	Consult QCO	Form 5, in raw data, or database report

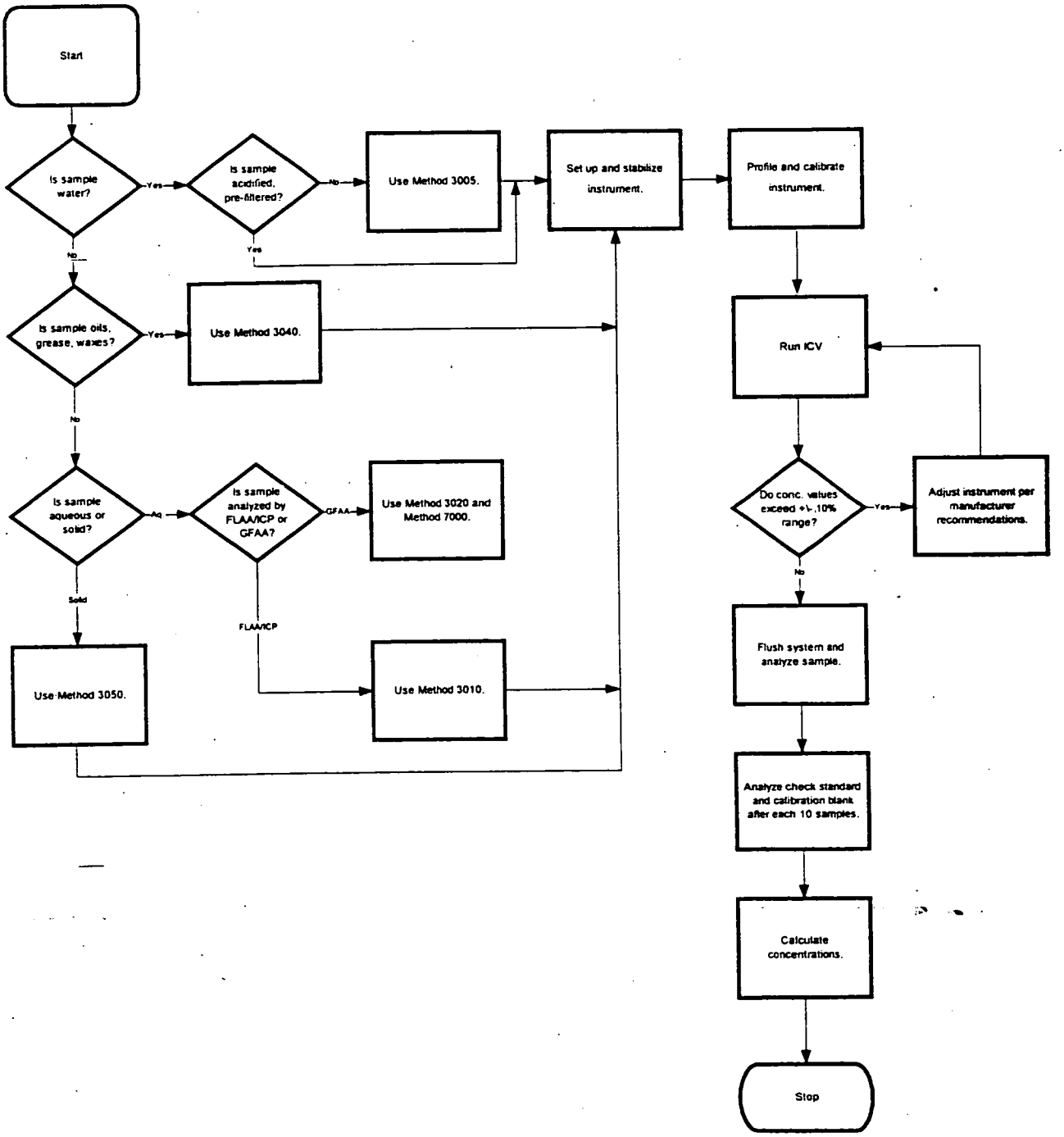
Laucks Testing Laboratories

Method 6010B QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Post Digestion Spike Recovery	75-125% used for new or unusual sample matrices	75-125%. Spike level either 2x RL or 2x native sample level, whichever is greater	used when MS is out of control	none	Form 5B, in raw data, or database report
Duplicate % Difference	± 20% if sample conc >10x the IDL	± 20% or current QC database criteria. ±RL if sample is <10x the IDL	5% or per batch	Consult QCO	Form 6, in raw data, or database report
Serial Dilution	± 10% difference used for new or unusual matrices	± 10% difference if sample conc > 50x the MDL	One/batch	Flag data with an "E".	Form 9 or in the raw data.
ICSA,AB	±20% true value of analytes, or ± the CRDL.	±20% true value of analytes, or ± the CRDL.	Beginning and end of run	Recalibrate and rerun affected samples	Form 4, or in raw data.
Standard Reference Material (SRM) Recovery	See QC control catalog	Control limits set by vendor	5% or per batch	Redigest samples	Form 7, in raw data, or database report

Appendix II

Flow Chart


Start
Is sample water?
Yes
Is sample acidified, pre-filtered?
No
Use Method 3005.
Yes
Set up and stabilize instrument.
Profile and calibrate instrument.
No
Is sample oils, grease, waxes?
Yes
Use Method 3040.
Run ICV
No
Is sample aqueous or solid?
Aq
Is sample analyzed by FLAA/ICP or GFAA?
GFAA
Use Method 3020 and Method 7000.
Do conc. values exceed +/-10% range?
Yes
Adjust instrument per manufacturer recommendations.
No
Solid
FLAA/ICP
Use Method 3050.
Use Method 3010.
Flush system and analyze sample.
Analyze check standard and calibration blank after each 10 samples.
Calculate concentrations.
Stop

Appendix III

Sample Handling and Preservation

Metals (except hexavalent chromium and mercury):

Measurement	Digestion Volume Required.	Collection Volume	Preservation/Holding Time
Total recoverable	100 mL	600 mL	HNO_3 to pH <2 6 months
Dissolved	100 mL	600 mL	Filter on site; HNO_3 to pH <2 6 months
Suspended	100 mL	600 mL	Filter on site 6 months
Total	100 mL	600 mL	HNO_3 to pH <2 6 months

Solid samples should be at least 200 g and usually require no preservation other than storing at 4°C until analyzed. Either plastic or glass containers may be used for sample collection.

Appendix IV

Analytical Sequence

Standard 0
Standard 1
ICV
ICB
CRDL Check
Linear Range Check
CCV
CCB
ICSAI
ICSABI
Sample #1
Sample #1D
Sample #1S
Sample #1L
Sample #2
Sample #3
Sample #4
ICSAF
ICSABF
CCV
CCB

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-7202

Title: Metals Analysis Using Inductively Coupled Plasma - Mass Spectrometry (ICP/MS), SW 846 Method 6020

Revision history:

Number	Date
1.0	04/26/95
2.0	02/09/98
3.0	4/22/98
4.0	7/22/99

Written by: _____ Date: 7-22-99
Ming-Hwa Hwang, Metals Supervisor

Approved by: _____ Date: 7-22-99
Harry Romberg, QA Officer

Approved by: _____ Date: 7-22-99
Kathy Kreps, Laboratory Director

Controlled Document

No. 20 Assigned to: Tetra

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1. Introduction and Scope

1.1 Method Description

Inductively coupled plasma-mass spectrometry (ICP-MS) is a technique which is applicable to µg/L concentrations of a large number of elements in water and wastes after appropriate sample preparation steps are taken. When dissolved constituents are required, samples must be filtered and acid preserved prior to analysis. No further digestion is required prior to analysis for dissolved elements. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial waste, soil, sludge, sediment, and other solid waste for which total (acid-leachable) elements are required.

See Appendix V for reporting limits.
See Appendix I for analytical masses and standard concentrations.

This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated their ability to perform the described analysis.

1.2 Sample Collection, Sample Storage, Holding Times

Water samples should to be collected in plastic or Teflon containers and preserved to a pH < 2. A one liter sample bottle is sufficient volume for analysis. Soil samples do not require preservation but need to be stored at 4° C and may be collected in glass if plastic containers are not available. At least 200 grams of sample should be collected. The holding time for metals is 6 months. If mercury is being analyzed by this technique, which is not currently approved or done without specific client arrangement, the holding time is 28 days.

1.3 Definition of Terms

This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

Batch Identifier - A number given to each analysis group which uniquely identifies that batch. This number is preceded by an "A", mmddyy, ICPMS, matrix (W for water, S for soil), sequence number (i.e. A022595ICPMSW01).

CCB - Continuing Calibration Blank - This is the same acronym used in the CLP program. This is a blank which is analyzed immediately after the CCV (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has maintained a stable baseline.

CCV - Continuing calibration verification. - This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has remained in calibration.

CLP - Contract Laboratory Program - The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.

DIW - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

ICB - Initial calibration blank - This term is borrowed from CLP. An instrument blank is made up in the same matrix as calibration standards, without target analytes.

ICV - Initial calibration verification - This term is borrowed from the CLP protocol. It is a standard which is analyzed at the start of each analytical run that is compared to the initial multi-point calibration to determine whether the instrument calibration is accurate.

IDL - Instrument detection limit. IDL's can be estimated by analyzing seven replicates of a standard analyte solution over three nonconsecutive days. The analyte concentration should be 3-5 times the estimated IDL. Multiplying the average standard deviation by three will yield the IDL for that analyte. Each measurement must be performed as though it were a separate analytical sample. IDL's must be determined quarterly

MDL - Method detection limit - The lowest concentration of an analyte which will yield a positive result that is greater than zero at a known level of confidence. MDLs are empirically determined and are performed annually.

LCS - Laboratory Control Sample. This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This

sample is used to demonstrate that the analytical system is in control. It may be considered to be a blank spike for most inorganic analyses and is preferred over artificially spiking blank materials.

Serial Dilution - If the analyte concentration is within the linear range of the instrument and is sufficiently high (minimally, a factor of 100 above the IDL/MDL), an analysis of a fivefold dilution must agree within ±10% of the original determination. If not, an interference effect must be suspected. One serial dilution must be analyzed for each twenty samples or less of each matrix in a batch. A serial dilution is denoted in the raw data by an "L".

ICSA - Interference Check Solution A. The ICSA is a solution that contains the interfering analytes. This solution is analyzed to indicate if a high level of interfering compounds will have an affect on the analytes of interest.

ICSAB - Interference Check Solution AB. The ICSAB is a solution that contains the interfering analytes and the analytes of interest. This solution is analyzed to indicate if a high level of interfering compounds will have an affect on the recovery of the analytes of interest.

Internal Standards - Internal standards are added to all blanks, standards, and samples. They monitor the affect of a sample's matrix on the quantification of the analytes of interest. The internal standards used are Sc45, In115, and Bi209.

Post-Digestion Spike - An analyte spike added to a portion of a prepared sample should be recovered to within 75% to 125% of the known value or within the laboratory derived acceptance criteria.

Standard-Addition - The standard addition technique involves adding known amounts of standard to an aliquot of the sample. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope than that of the calibration standards.

QC Period - Quality control period - An analysis sequence initiated by the analysis of one or more standards, followed by samples, and terminated with a standard and blank analysis. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP

RSD or %RSD - Relative standard deviation or percent relative standard deviation - The ratio of the standard deviation of a set of values to the mean of the set of values. A measure of the similarity of the values one to another.

2. Equipment List and Standards

2.1 Instrumentation:

Perkin-Elmer ELAN 5000

2.2 Standards

SW 846 requires the use of one standard and a blank. Standards are made in a 1% HNO_3. See Appendix I for standard concentrations.

2.3 Internal Standards

Sc45, In115 and Bi209 are used as internal standards.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

All standards, samples and sample solutions should be handled as if they are hazardous substances.

Refer to the instrument manufacturer's manual for routine instrument precautions.

Routine precautions include an awareness of the moving parts on the instrument you are using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

Electrical shock - All instruments present the possibility of electrical shock The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

Radio Frequency - The ELAN 5000 uses a high energy RF. Although the generator is well shielded, care should be taken when operating the instrument. Pace makers can be adversely affected by exposure to high energy RF.

Plasma Radiation - Do not view the torch without the proper eye wear. Severe eye damage can occur if the plasma is viewed directly.

3.2 Waste Disposal

Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on waste segregation and disposal.

4. Quality Control

4.1 Method Detection Limit Study

Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in the Laucks SOP on performing MDL studies. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration approximately 3 to 5 times the estimated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL.

4.2 Linear range study

Linear ranges for each analyte are determined by analyzing a high concentration "sample". The analytically determined concentration must be within 5% of the true value. The true value is the upper limit of the ICP/MS linear range. Linear ranges must be verified quarterly.

4.3 Internal Standards

A 50 uL aliquot of a 20 ppm of Sc45, 10 ppm of In115 and 10 ppm of Bi209 is added to a 10 mL of all standards and samples prior to analysis.

Criteria

The intensities of all internal standards for instrument check standards must be between 80 and 120 percent of the intensities of the internal standards in the initial calibration standard.

Corrective action

If the criteria are not met, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and re-analyze the affected samples.

Criteria

The intensities of all internal standards in the samples must be between 30 and 120 percent of the intensities of the internal standards in the initial calibration standard.

Corrective action

When the intensity of any internal standard in the sample fails to fall between the required levels, the sample must be diluted fivefold (1+4) and re-analyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until all internal standards fall within the prescribed windows.

4.4 Initial Calibration

Analyze standard solutions using a minimum of a calibration blank and one standard. The calibration curve must be verified by running an Initial Calibration Standard (ICV) and obtaining agreement within 10% of the expected concentration.

Criteria and Corrective Action:

Since a linear regression is not possible when using a two point calibration on the ELAN 5000, the standard curve is validated by evaluating the ICV and the subsequent CCVs. If the corresponding control limits for the ICV and CCV are exceeded, then the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable ICV, CCV must be reanalyzed..

4.5 Initial Calibration Verification

Immediately after the calibration curve, analyze a standard from a source other than that from which the calibration material was obtained.

Criteria

The calculated concentration of the ICV should be within 90%-110% of the true value.

Corrective action

If the ICV criteria are not met, the analysis is terminated. Perform system maintenance and re-calibrate the instrument.

4.6 Initial Calibration Blank

After the analysis of the ICV standard an instrument blank (ICB) is analyzed. The levels of target analytes in the ICB should not exceed the contract required detection limit .

Corrective action

If the initial ICB contains target analyte levels above the contract required detection limit, the system is out of control. The source of contamination must be identified and corrected before proceeding with the analysis.

4.7 Continuing Calibration Verification (CCV) and Blank (CCB)

A continuing calibration verification standard is analyzed after every 10 samples. Immediately following the CCV, a blank solution is analyzed. In addition, this standard and blank must be the last samples analyzed in the run.

Criteria

The CCV must fall within ± 10% of the true value.

The levels of target analytes in the CCB should not exceed the contract required detection limit.

Corrective action

If CCV limits are exceeded, check calculations or perform instrument maintenance. Recalibrate and reanalyze. No sample results may be reported that are not bracketed by a successful calibration and a CCV which is in control or by preceding and following CCVs which are within limits.

If the initial CCB contains target analyte levels above the contract required detection limit, the system is out of control. The source of contamination must be identified and corrected and the affected samples re-analyzed. As with the CCVs, no sample results may be reported that are not bracketed by a successful initial and continuing calibration blank which are in control or by preceding and following CCBs which are within limits.

4.8 Interference Check Solutions A (ICSA) and AB (ICSAB)

Due to the high sensitivity of the ICP-MS technique and instrument developments that have occurred since the method was written, the high dissolved solids content of the specified ICS

solutions are not recommended by the manufacturer for modern instruments. The ICSA and ICSAB solutions are prepared at different concentration levels from method 6020 to avoid clogging of the sampler cone orifice and damage to the instrument. Therefore, Al, Ca, Fe, Mg, Na, P, K, S, C, and Cl in the ICSA and the ICSAB are at 1/10 of the specified levels. See Appendix II for ICSA and ICSAB solutions concentrations.

(ICSA):

At the beginning and at the end of each run, an interference check solution A is analyzed. This solution contains interfering elements only. All other elements are not present in the solution. All elements not present should show a recovery of zero, or ± the contract required detection limit.

Corrective Action:
If the analytes do not recover within the specified control limits, then the system is out of control. The problem needs to be identified and corrected prior to beginning another run.

(ICSAB):

At the beginning and end of each analytical sequence an ICSAB must be analyzed. Analytes must recover between 80-120%.

Corrective Action:

If the analytes do not recover within the specified control limits, then the system is out of control. The problem needs to be identified and corrected prior to beginning another analysis.

4.9 Method Blanks

Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time or at least one blank every 20 samples, which ever is more frequent. Any analyte response above the CRDL is reported. For a method blank to be acceptable for use with the accompanying samples, the concentration of the blank of any analyte of concern should not be higher than the highest of either:

(1) The reporting limit, or
(2) Five percent of the regulatory limit for that analyte, or
(3) Five percent of the measured concentration in the sample.

Corrective Action:

Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if an analyte were found in the blank but not in any of the associated samples then sample group may not require re-analysis. In any case, if re-preparation and re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Control Officer. It is the laboratory's responsibility to ensure that method interference caused by contaminants in acids, solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the analytical run be minimized. In the extreme case of chronic contamination, blanks may have to be analyzed from each stage of the sample processing to determine the contamination source so it can be eliminated. In all cases where blank contamination exceeds the control limit, a narrative comment must be made which documents the corrective actions taken.

4.10 Laboratory Control Sample

The LCS is made from an independent source of the same matrix (soil or water) and is carried through the entire digestion procedure. An LCS is performed with each digestion batch. At a minimum, LCSW(water) control limits are 80% to 120%.

LCSS(soil) control limits are supplied by the manufacturer. LCSS control limits are not derived by the laboratory due to the small number of data points available from each lot of certified material.

Corrective Action

If the LCS is not within the required control limits, a redigestion will occur for the affected analytes.

4.11 Matrix Spike

A sample is chosen at random from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to preparation. The analyst should attempt to avoid selecting samples which are identified by the client as blanks. As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may also avoid selecting the most difficult sample of the batch for spiking. The minimum frequency for MS analysis is 1 each per 20 samples per matrix. This will be best accomplished by running one with every batch for many analyses. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$recovery,\% = \frac{(SS - S)}{SA} * 100$$

where:

SS = concentration in spiked sample
S = native concentration in unspiked sample
SA = spike added, the amount of spiking material actually added calculated on the sample basis.

For ICP/MS, control limits for spike recoveries will be 75-125% unless the sample result is greater than 4 times the spike concentration or unless otherwise specified in the project specific QAPP. In-house control limits are based on historical performance.
The recovery criteria are detailed in the QC Database QC_DB and will change from time to time.

Corrective Action:

Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action will first involve recalculation, followed by possible re-preparation, and/or reanalysis. This process should also look at the recovery of matrix spiking compounds from the SRM and/or blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken. Data reported in validatable packages will be flagged with an "N" indicating the out-of-control event.

4.12 Post-Digestion Spike

A post digestion spike is also performed to a portion of a prepared sample. The minimum frequency for MS analysis is 1 each per 20 samples per matrix, control limits for post-spike recoveries will be 75-125%

Corrective Action:

Samples with post-spike recoveries outside control limits will be diluted and re-analyzed to compensate for matrix effects. The results must agree to within 10% of the original measured concentrations. A standard-addition technique may also be used to compensate for matrix effects.

4.13 Matrix Spike Duplicate/Sample Duplicate

Method QC consists of MS/MSD. A duplicate maybe be performed instead of a MSD. Other types of QC can performed at the client's request.

Criteria

At least one matrix spike duplicate sample per 20 samples per matrix is required when matrix spikes are being performed. RPD values are calculated in a manner similar to MS/MSD RPDs:

$$RPD = \frac{|SS - SSD|}{(SS + SSD)/2} * 100$$

where:
SS = concentration in spiked sample
SSD = concentration in matrix spiked duplicate sample

For sample concentrations greater than 5 times the CRDL, control limits for RPD of duplicates will be ±20% unless otherwise specified in the project specific QAPP. For sample concentrations less than 5 times the CRDL, control limits for the difference will be ± the CRDL. In-house control limits are based on historical performance. The RPD control limits are detailed in the current QC Database QC_DB and will change from time to time.

Corrective Action:

If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer. In a validatable package, data associated with an out-of-control RPD will be flagged with an "*".

4.14 Serial Dilution

A five-fold dilution is performed on the QC sample in each analytical batch. The difference between the initial value and the serial dilution should agree within 10%. If the difference is greater than 10% on analytes that exhibit a level 50 times greater than the IDL, then results for those analytes will be flagged with an "E".

Corrective Action:

No corrective is necessary other than appropriately flagging the data.

5. Procedure

5.1 Instrumental Conditions

- Refer to manufacture's instruction for specific operating procedures. Allow at least 30 minutes for the instrument to stabilize before initiating any analysis.

- Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any sample being analyzed. The monitored masses of Mg, Rh, and Pb must meet the following criteria:

Element	RSD for replicate (minimum of four) integrations.	Mass, amu	Resolution @ 10 % peak height, amu
Mg	< 5%	23.90-24.10	<0.9
Rh	< 5%	102.80-103.00	<0.9
Pb	< 5%	207.90-208.10	<0.9

5.2 Analytical Operation

- Calibrate the instrument, using a calibration blank and a standard. Refer to Appendix I for the applied levels of concentration.

- All masses which could affect data quality are monitored to determine potential effects from matrix components on the analytes of interest.

- After the calibration has been established, an ICV solution is analyzed to verify the validity of the curve. Measurements for the analytes of interest must be at ±10% of the true value. A re-calibration and re-analysis is required for any analyte which falls outside the control limit.

- Analyze the interference check samples (ICSA and ICSAB) prior to and after the analysis of samples

- Analyze a CCV and a CCB once every 10 analytical samples.

- Dilute samples that exceed the established linear range of the instrument.

6. Reports

6.1 Data Packet Organization

- See the SOP metals validation for a check list detailing data packet organization
- If requested, all analysis performed under SW 846 guidelines the data can be reported via CLP SOW 3/90 forms.
- Data packages will be produced via Enviroforms. Analyte levels that are less than the MDL will be reported as the SDL followed by a "U". Analyte levels that fall between the MDL and the reporting limit will be flagged with a "B". Analyte levels greater than or equal to the reporting limit PQL will be reported without a flag.

CODE	Definition	
U	The analyte of interest was not detected, to the limit of detection indicated.	❁◆
B	The analyte of interest was detected between the MDL and the reporting limit.	❁
N	The spike recovery exceeded the control limits.	❁
*	The duplicates exceeded the RPD control limit or their difference exceeded the reporting limit.	❁
E	The Serial Dilution did not agree within 10%.	❁
S	The analyte concentration was determined by MSA.	❁

◆ Used in all reports.
❁ Used in data validatable packages.

6.2 References:

Test Methods for Evaluating Solid Waste, SW-846, Method 6020, Revision 0, September 1994

Appendix I

Standard Solutions

Elements	Mass	STD, µg/L
Be	9	50
Na	23	500
Mg	26	500
Al	27	400
K	39	500
Ca	44	500
V	51	100
Cr	52	100
Mn	55	150
Fe	54,57	200
Co	59	100
Ni	60	400
Cu	63,65	50
Zn	66	200
As	75	100
Se	82	200
Ag	107	100
Cd	111	50
Sb	121	60
Ba	137	400
Tl	205	100
Pb	208	50
Li	7	200
B	11	200
Mo	98	200
Sn	118,120	200
U	238	250

The STD is made by diluting 10.0 mL of the ICP/MS stock standard to a 100 mL final volume.

The ICP/MS stock standard which consists of:

100 µL	ICAL-1
1000 µL	ICAL-2
200 µL	ICAL-3
1000 µL	ICAL-4
100 µL	ICAL-5
250 µL	1000 ppm U
200 µL	1000 ppm B
200 µL	1000 ppm Mo
200 µL	1000 ppm Li
200 µL	1000 ppm Sn
40 µL	1000 ppm Be
150 µL	1000 ppm Se

Note: 50 µL of 20 ppm Sc45, 10 ppm In115 and 10 ppm Bi209 is added to a 10 mL aliquot of standard.

Appendix II

ICSA and ICSAB Solutions

Element	ICSA (PPM)	ICSAB (PPM)
Aluminum	4	4
Arsenic		0.020
Cadmium		0.020
Calcium	12	12
Chromium		0.040
Cobalt		0.040
Copper		0.040
Iron	10	10
Magnesium	4	4
Manganese		0.040
Molybdenum		0.16
Nickel		0.040
Potassium	4	4
Selenium		0.020
Silver		0.040
Sodium	10	10
Vanadium		0.040
Zinc		0.020

Appendix III

QC Summary Table

Laucks Testing Laboratories

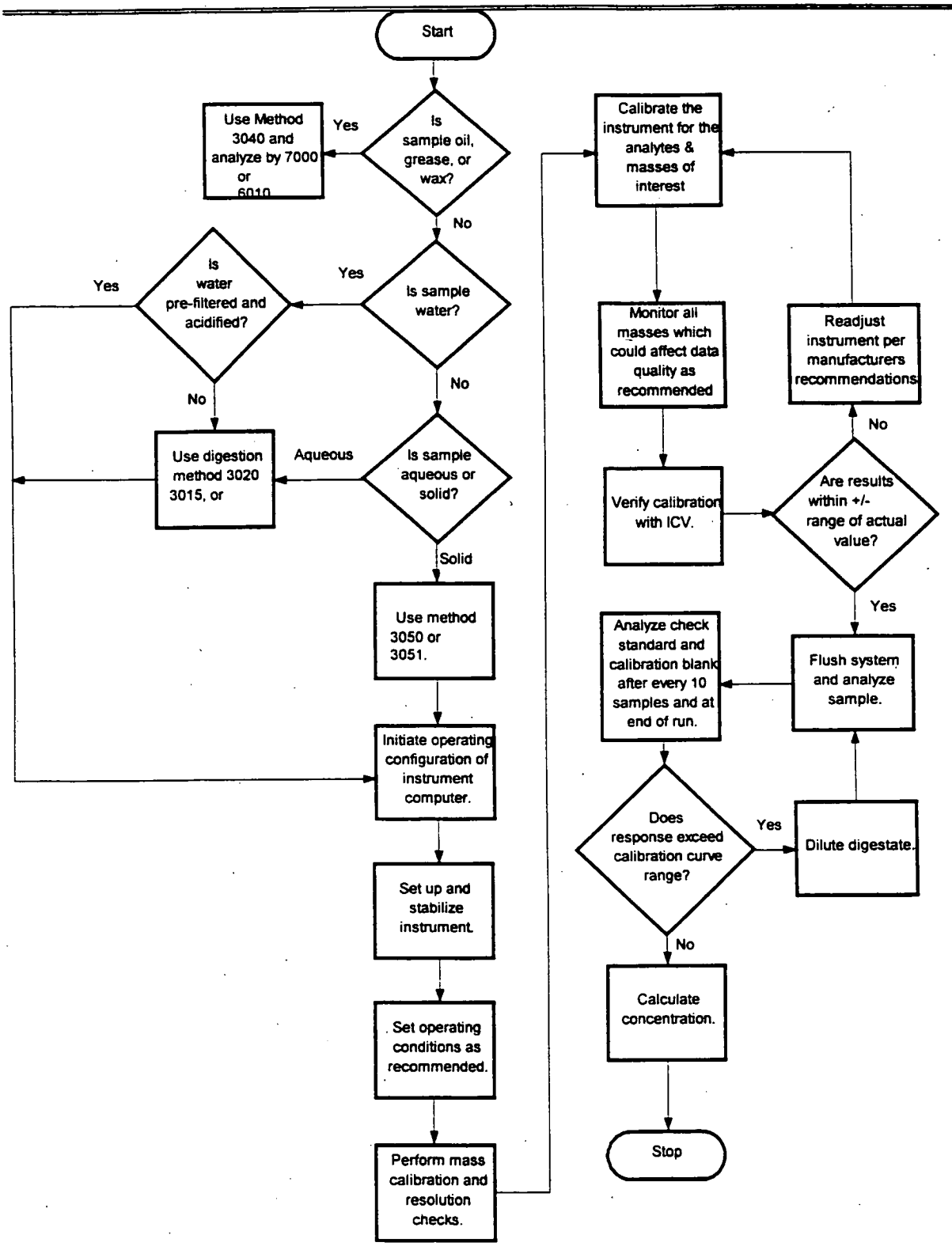
Method SW 846 6020 QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Mass Calibration Check	must be performed in mass regions of interest and be within ±0.1 amu of the actual value.	Mg 23.90-24.10 Rh 102.80-103.00 Pb 207.90-208.10	Beginning of each analysis.	Perform new mass calibration.	Instrument Logbook
Resolution Check	< 0.9 amu full width at 10% peak height	< 0.9 amu full width at 10% peak height	Beginning of each analysis.	Adjust resolution.	Instrument Logbook
Initial Calibration	Blank and at least one standard	Blank and one standard	Beginning of each analysis	NA	In the raw data and/or on FORM 14.
Initial Calibration Verification	±10% of true value. Made from an independent source.	±10% of true value. Made from an independent source..	Immediately following calibration.	Recalibrate and reverify.	Form 2, in the raw data
Initial Calibration Blank	Values must be < 3x the IDL for each element.	Values must be < CRDL	Immediately following ICV.	Recalibrate, reverify, and rerun the ICB.	Form3, in the raw data
Continuing Calibration Verification	±10% true value.	±10% true value. Analyte levels are at the mid-range of the calibration.	Every 10 samples and end of run.	Recalibrate and rerun affected samples.	Form 2, in the raw data
Continuing Calibration Blank	Values must be < 3 times the IDL for each element.	Values must be < CRDL	Immediately following CCV.	Recalibrate and rerun affected samples.	Form 3, in the raw data
Method Blank	< CRDL or <5% of regulatory limit or any sample	< CRDL or <5% of regulatory limit or any sample	One/batch	Redigest samples	Form 3, in the raw data.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Internal Standards	1.Samples: 30 % - 120 % of the initial calibration standard 2. Instrument Check Standards: 80 -120 of the initial calibration standard.	1. Samples 30 % - 120 % of the initial calibration blank. 2. Instrument Check Standards: 80 -120 of the initial calibration blank.	1. All samples 2. All instrument check standards	1. dilute and reanalyze. 2. recalibrate, re-analyze the affected samples.	In the raw data.
Serial Dilution	within ±10% of the original value if the analyte conc. is > 100 x the IDL.	within ±10% of the original value if the analyte conc. is > 100 x the IDL.	One/batch	Flag data with an "E".	Form 9,.in the raw data
Duplicate, % Difference	± 20% for analyte values greater than 100 times the IDL.	± 20% or current QC database criteria.	5% or per batch	reanalyze digestates, if still fail, consult QCO	Form 6, in raw data, or database report
Matrix Spike Recovery		75-125% or current QC database criteria.	5% or per batch	Consult QCO	Form 5A, in raw data, or database report
Post-Digestion Spike	75%-125%	75%-125%	5% or per batch	dilute and re-analyze or MSA	Form 5B, in the raw data
Laboratory Control Sample	One/batch, no acceptance criteria	LCSW: 80%-120% LCSS: Manufacturer Specs.	One/batch	Redigest samples.	Form 7, in raw data, or database report
ICSA and ICSAB	±20% true value of analytes, or ± the CRDL.	±20% true value of analytes, or ± the CRDL.	Beginning and end of run	reanalyze affected samples	Form 4, or in raw data.

Appendix IV

Flow Chart


Start
Is sample oil, grease, or wax?
Yes
Use Method 3040 and analyze by 7000 or 6010
No
Is sample water?
Yes
Is water pre-filtered and acidified?
Yes
No
Use digestion method 3020 3015, or
No
Is sample aqueous or solid?
Aqueous
Solid
Use method 3050 or 3051.
Initiate operating configuration of instrument computer.
Set up and stabilize instrument.
Set operating conditions as recommended.
Perform mass calibration and resolution checks.
Calibrate the instrument for the analytes & masses of interest
Monitor all masses which could affect data quality as recommended
Verify calibration with ICV.
Are results within +/- range of actual value?
No
Readjust instrument per manufacturers recommendations
Yes
Flush system and analyze sample.
Analyze check standard and calibration blank after every 10 samples and at end of run.
Does response exceed calibration curve range?
Yes
Dilute digestate.
No
Calculate concentration.
Stop

Appendix V

Routine Reporting Limits

SW 846 6020 Reporting Limits

Element	Reporting Limit, µg/L	Element	Reporting Limit, µg/L
Ag	3.0	Mn	1.0
As	1.0	Mo	10.0
B	10.0	Ni	10.0
Ba	2.0	Pb	1.0
Be	1.0	Sb	1.0
Cd	1.0	Se	3.0
Co	3.0	Sn	10.0
Cr	5.0	U	100
Cu	2.0	V	2.0
Li	10.0	Zn	10.0

Reporting limits are approximately 2-10 times the instrumental MDL. The MDL is based on samples prepared using SW 846 3015. Values actually reported may be less than the routine reporting limits but above our method detection limit.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-7501

Title: **Operation of the PE FIMS 400 for the Analysis of Hg**

Revision history:

Number	Date
1	02/04/98
0	02/14/96

UNCONTROLLED

Revised by: Bill Lundberg
Bill Lundberg, Inorganics Division Manager
Date: 2/5/98

Approved by: Harry Romberg
Harry Romberg, QC Officer
Date: 2-5-98

Approved by: Karen J. Kotz
Karen Kotz, Laboratory Director
Date: 2/5/98

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1. Introduction and Scope

1.1 Method Description:

1.1.1 This SOP covers the cold vapor analysis of Hg by the Perkin-Elmer Flow Injection Mercury System, Model 400 (FIMS 400). Sample handling and preparation are as required by SW 846 methods 7470 and 7471. This SOP is also valid for the preparation and analysis of samples under CLP protocol when used in conjunction with the SOW ILM04.0. Where the requirements of these procedures differ, the most stringent requirements are used. The requirement of analyzing soil samples in triplicate under 7471 is not used except on request.

1.1.2 After preparation and digestion to convert Hg to its ionic form, 0.5 mL of sample is introduced into a stream of carrier solution (3% HCl), mixed with a $SnCl_2$ suspension to reduce the Hg ion to its metallic form, which is then carried into an adsorption tube through which passes light at a wavelength of 253.7 nm. The adsorption is then measured.

1.1.3 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1 Samples are stored either in glass or plastic. The holding time is 28 days from collection. Soil samples are stored at 4° C±2° C. Water samples are stored at room temperature. Water samples are preserved by the addition of HNO_3 to a pH <2.

1.3 Definition of Terms

1.3.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

1.3.2 LFB - Laboratory Fortified Blank - A sample of DIW to which a known amount of Hg is added.

1.3.3 CCB - Continuing Calibration Blank - This is the same acronym used in the CLP program. This is a blank which is analyzed immediately after the CCV (almost always

after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has maintained a stable baseline.

1.3.4 CCV - Continuing calibration verification. - This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has remained in calibration.

1.3.5 CLP - Contract Laboratory Program - The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.

1.3.6 Corr Coef, CC - Correlation coefficient - A measure of the "goodness of fit" of a set of data to a linear regression model. The closer the value is to 1, the higher the degree of confidence in the correlation

1.3.7 DIW - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

1.3.8 ICB - Initial calibration blank - This term is borrowed from CLP. An instrument blank is made up in the same way as calibration standards, without target analytes.

1.3.9 ICV - Initial calibration verification - is a standard which is analyzed at the start of each analytical run that is compared to the initial multi-point calibration to determine whether the instrument calibration is accurate. This verification standard is from a source different from that used to make the calibration standards

1.3.10 IDL - Instrument detection limit. The lowest concentration of a target analyte that will yield a signal:noise ratio of least 3x. Determined quarterly using blanks to which a known quantity of standard has been added. The IDL is determined by analyzing 7 replicates spiked at 2-5 times the expected IDL on three non-consecutive days. The sum of the standard deviations of the three runs is the IDL.

1.3.11 MDL - Method detection limit - The lowest concentration a sample which will yield a positive result that is greater than zero at a known level of confidence. MDLs are empirically determined by Laucks annually.

1.3.12 MDL standard - Method detection limit standard - A standard prepared so that the concentration of Hg is 1-5 times the anticipated MDL

1.3.13 LCS - Laboratory Control Sample - A sample containing a known quantity of Hg used to verify digestion and analysis. LCSW indicates a water sample. It is used interchangeably with ICV. LCSS indicates a soil sample.

1.3.14 RSD or %RSD - Relative standard deviation or percent relative standard deviation - The ratio of the standard deviation of a set of values to the mean of the set of values. A measure of the similarity of the values one to another.

1.3.15 PBW - A blank carried through the sample preparation and digest procedures.

2. Equipment, Standards and Reagents

2.1 Equipment

2.1.1 Equivalent equipment may be used where appropriate.

FIMS 400 automatic Hg analyzer.
Perkin Elmer AS-90 autosampler.
Epson LQ300 dot-matrix printer.
Wells 18"X24" hot water bath.
BOD bottles
Analytical balance
Micropipettes: 25, 50, 100, 200, 500 and 1000 µl.
50 mL and 15 mL centrifuge tubes - polystyrene.

2.2 Standards

2.2.1 All standards must be prepared in 0.15% HNO_3.

2.2.2 Intermediate Hg solution: Dilute 100 µl of 1000 ppm Hg standard solution to 100 mL in DIW to which 0.15 mL HNO_3 has been added. The identification number of the standard solution used and the dilution must be entered on the digestion log (Appendix II). This solution must be prepared daily. Since the intermediate and working standards are prepared daily, they are not recorded in the standards logbook.

2.2.3 0.2 µg/L standard - Place 100 mL DIW in a BOD bottle. Add 20 µl stock Hg solution

2.2.4 0.5 µg/L standard - Place 100 mL DIW in a BOD bottle. Add 50 µl stock Hg solution.

2.2.5 1.0 µg/L standard - Place 100 mL DIW in a BOD bottle. Add 100µl stock Hg solution.

2.2.6 2.0 µg/L standard Place 100 mL DIW in a BOD bottle. Add 200 µl stock Hg solution.

2.2.7 5.0 µg/L standard - Place 100 mL DIW in a BOD bottle. Add 500 µl stock Hg solution.

2.2.8 10.0 µg/L standard - Place 100 mL DIW in a BOD bottle. Add 1000 µl stock Hg solution.

2.2.9 ICV solution - Add 100 mls DIW to a BOD bottle. Add sufficient stock ICV solution to produce a concentration of 1.0 to 5.0 µg/L.

2.2.10 CCV/CCB/LFB - In setting up the run, use the 5.0 µg/L standard for the CCV and LFB; for the CCB use the calibration blank.

2.2.11 MS/MSD - Add 100 µl intermediate Hg solution to the samples being spiked. When performing Hg under CLP protocols use 100 µl intermediate Hg solution and perform MS/Duplicate.

2.2.12 LCSS - Laboratory control soil sample. Concentrations and limits are certified by the manufacturer.

2.3 Reagents:

2.3.1 DIW - deionized water free of impurities.

2.3.2 H_2SO_4 (sulfuric acid) - concentrated, reagent grade

2.3.3 HNO_3 (nitric acid) - concentrated, reagent grade

2.3.4 HCl (hydrochloric acid) - concentrated, reagent grade

2.3.5 Stannous chloride - Add 11 g. $SnCl_2 \cdot 2H_2O$ (stannous chloride dihydrate) to 1 L DIW to which has been added 30 mL concentrated HCl.

2.3.6 $KMnO_4$ (potassium permanganate) - Dissolve 100 g. $KMnO_4$, marked "suitable for Hg determination", in 2 L DIW. This is a saturated solution. Sufficient undissolved $KMnO_4$ should be allowed remaining in the bottom of the bottle to assure a saturated solution.

2.3.7 $K_2S_2O_8$ (potassium persulfate) - Dissolve 50 g. $K_2S_2O_8$, marked "suitable for Hg determination", in 1 L DIW. This is a saturated solution. Sufficient undissolved $K_2S_2O_8$ should be allowed remaining in the bottom of the bottle to assure a saturated solution.

2.3.8 $NaCl/NH_2OH{\cdot}HCl$ (sodium chloride/hydroxylamine hydrochloride) - Dissolve 240 g NaCl (table salt is generally used) and 240 g. $NaCl/NH_2OH{\cdot}HCl$ (reagent grade marked "suitable for Hg determination") in 2 L DIW. Contamination has been experienced with this solution. For this reason a 50% solution should be analyzed by the FIMS 400 whenever a new bottle is made up. If the absorbance (peak height) exceeds .004 the container of $NaCl/NH_2OH{\cdot}HCl$ should be marked "Contaminated" and disposed of.

2.3.9 Carrier solution - The carrier is a 3% HCl solution.

3. Safety Precautions and Waste Disposal:

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.4 Electrical shock - All instruments present the possibility of electrical shock The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.5 Because of the toxic nature of Hg vapor, inhalation or skin contact should be avoided.

3.1.6 The usual precautions should be taken in handling acids.

3.1.7 $SnCl_2$ is a skin and eye irritant; avoid contact.

3.1.8 The addition of hydroxylamine after digestion releases gas, including chlorine. Avoid inhalation; use hood if necessary.

4. Calibration and Quality Control

4.1 Method Detection Limit Study (MDL).

4.1.1 MDL studies for Hg water samples and soil samples are performed annually. Consult the current SOP on MDL determinations for specifics.

4.2 Initial Multi-Point Calibration:

4.2.1 Concentrations:

Standard Name	Concentration
S0	0.0 µg/L
S0.2	0.2 µg/L
S0.5	0.5 µg/L
S1.0	1.0 µg/L
S2.0	2.0 µg/L
S5.0	5.0 µg/L
S10.	10.0 µg/L

Standards are made fresh daily from the intermediate standard in 0.15% HNO_3.

4.2.2 The calibration blank, the ICV, the LCS, the LFB, the ICB and all standards are digested along with the samples being analyzed.

4.3 Calibration Criteria

4.3.1 Calibration curve - CC must be greater than 0.995.

4.3.2 ICV - For CLP analyses the limits are 80-120 %, for SW 846 the limits are 90-110%.

4.3.3 ICB - Limitations presently in use are -0.2 µg/L to 0.2 µg/L .

4.3.4 A PBW and an LFB are run immediately following the successful calibration. The limitations on the PBW are the same as the limitation on the ICB. The limitations on the LFB are as set forth in QC-DB.

4.3.5 If the above criteria are not met, recalibration must be performed.

4.4 Continuing quality control:

4.4.1 A CCV followed immediately by a CCB must be run every 10 samples and after the last sample. The ICB, PBW and LFB count as samples for this purpose.

4.4.2 Criteria - For CCV's the limitations are 80% to 120%. For blanks the limitations are -0.2 µg/L to 0.2 µg/L .

4.4.3 Corrective action - If a CCV or CCB are out of control, a recalibration must be performed followed by a reanalysis of all samples since the last previous successful CCV and/or CCB.

4.5 Matrix Spike

4.5.1 A sample is chosen at random from the samples to be analyzed, and 100 µl of intermediate standard is added. The spike level is then 1.0 µg/L. The analyst should attempt to avoid selecting samples which are identified by the client as blanks. As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may also avoid selecting the most difficult sample of the batch for spiking. It is not always required that a matrix spike analysis be performed with each preparation/analysis batch, however, the minimum frequency for MS analysis is 1 each per 20 samples per matrix. This will be best accomplished by running one with every batch for many analyses. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$\text{recovery,\%} = \frac{(SS - S)}{SA} * 100$$

where:
SS = concentration in spiked sample
S = native concentration in unspiked sample
SA = spiked added, the amount of spiking material actually added to the sample calculated on the sample basis

4.5.2 The recovery criteria are listed in QC_DB and will change from time to time.

4.5.3 Corrective action

4.5.3.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action will first involve recalculation, followed by possible re-preparation, and/or reanalysis. This process should also look at the recovery of Hg from the SRM and/or blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.6 Matrix Spike Duplicate

4.6.1 The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values. This calculation is as follows:

$$RPD = \frac{|S1 - S2|}{(S1 + S2)/2} * 100$$

where:
S1 = measured concentration for MS sample
S2 = measured concentration for MSD sample

4.6.2 RPD control limits are listed in QC_DB and will change from time to time.

4.7 Sample Duplicate

4.7.1 Sample duplicates are required when CLP practices are employed, or when the method specifically calls for duplicates. At least one duplicate sample per 20 samples per matrix is required when matrix spikes are being performed.

$$RPD = \frac{|S1 - S2|}{(S1 + S2)/2} * 100$$

where:
S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analyses

4.7.2 The RPD control limits listed in QC_DB and will change from time to time.

4.7.3 Corrective action

4.7.3.1 If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that

sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation Procedures:

5.1 Digest - BOD bottles - Soil or Water:

5.1.1 Digestion log (Appendix II): The digestion log should show the sample numbers, the date, the name of the analyst, the time placed in the hot water bath, the time when the temperature reached 95± 5° C, and the time removed from the hot water bath. One should be prepared for each run. An example is attached as Appendix II. The numbers of each BOD bottle must be placed in the leftmost column of this form to identify which sample is in each BOD bottle.

5.1.2 Preparation of standards:

5.1.2.1 Prepare an intermediate standard daily by adding 100 µl of the 1000 mg/L stock standard to 100 mL of 0.15% HNO_3 in DIW, giving a concentration of 1.0 mg/L of Hg.

5.1.2.2 Place 100 mL DIW in each of 9 BOD bottles.. Mark these BOD bottles with the concentration of each standard in µg/L , plus one marked "Blank", one marked "ICV" and one more marked ICB.

5.1.2.3 Add from the intermediate standard the following amounts to the following BOD bottles:

0 µg/L	0 µl
0.2 µg/L	20µl
0.5 µg/L	50 µl
1.0 µg/L	100 µl
2.0 µg/L	200 µl
5.0 µg/L	500 µl
10.0 µg/L	1000 µl

5.1.2.4 To the ICV BOD bottle add that amount of the ICV standard which will produce a concentration from 1.0 µg/L to 5.0 µg/L .

5.1.2.5 The standards, the ICV and the ICB must be digested along with the PBW, LFB and samples.

5.2 Digestion - Water Samples

5.2.1 Place 100 mL DIW in the PBW BOD bottle.

5.2.2 Place 100 mL DIW + 100 µl intermediate standard in the LFB BOD bottle.

5.2.3 Place 100 mls sample in the BOD bottle designated for that sample, being sure to place 100 mL sample in the designated duplicate, MS and MSD BOD bottles for the sample involved. TCLP samples and spikes should be diluted 20 mL/100 mL (dilution factor of 5) in DIW. The TCLP spikes should be diluted 2 mL/100 mL in DIW.

5.2.4 Add the required quantity (See Sec. 4.5.1) of intermediate standard to the MS and MSD BOD bottles.

5.2.5 Add the following reagents to each BOD bottle:

5 mL concentrated H_2SO_4
2.5 mL concentrated HNO_3
15 mL $KMnO_4$ solution
8 mL $K_2S_2O_8$ solution

5.2.6 The $KMnO_4$ color must persist for 15 minutes. If it does not, more $KMnO_4$ must be added.

5.2.7 Place all the BOD bottles, being careful to keep them in order, in the hot water bath in a hood, and record the time on the digest log. Monitor the temperature of the hot water bath and record the time when the temperature reaches 90° C. Continue to heat the water bath, keeping the bath at 95 ± 5 C for two hours.

5.2.8 Remove the BOD bottles from the hot water bath and allow to cool.

5.2.9 Add 6 mL $NaCl/NH_2OH{\cdot}HCl$ solution and mix until the mixture clears. If some undissolved permanganate remains, it will usually disappear on standing after a few minutes.

5.3 Digestion - Soil samples:

5.3.1 Place 100 mL DIW in the PBW BOD bottle.

5.3.2 Place approximately 0.5 g., or, for certain CLP and 846 analyses, approximately 0.2 g of sample in each of the BOD bottles to which that sample applies. Record the exact weight on the digestion log.

5.3.3 Add 3.75 mL HCl , 1.25 mL HNO_3 and 5 ml DIW to each BOD bottle.

5.3.4 Place all BOD bottles in a hot water bath in a hood that is at 95° C ± 5° C. Maintain the heat at this level for 2 minutes.

5.3.5 Cool for a few minutes and add 50 mL DIW and 15 mL $KMnO_4$. Mix.

5.3.6 The $KMnO_4$ color must persist for 15 minutes. If it does not, more $KMnO_4$ must be added.

5.3.7 Place all BOD bottles in a hot water bath that is at 95° C ± 5° C. Record the time on the digest log. Maintain the hot water bath at this temperature for 30 minutes. Remove the BOD bottles and allow to cool.

5.3.8 Add 6 mL $HCl/NH_4NH_2OH{\cdot}HCl$ solution and mix to remove color.

5.3.9 Add 50 mL DIW. Allow to cool.

5.4 Analysis on FIMS 400.

5.4.1 This is a programmed analysis. The method name is "hg_cv" (Appendix V). This is a 6 point curve with a blank correction. The development of the calibration curve, including the ICV and ICB, is automatic. If the calibration is unsuccessful, recalibration is attempted. If a standard is seriously out of line, it is ignored by the Perkin-Elmer software. The 5.0 µg/L standard is used for CCV's; the calibration blank for CCB's, both of which are programmed to be run every 10 samples. If a CCV or a CCB fails to meet quality control specifications, the system recalibrates and reruns all samples since the last preceding valid CCV or CCB. A CCV and a CCB are also run after the last sample in the run.

5.4.2 Sample Information sheet - Appendix IV.

5.4.2.1 Click the automatic analysis button on the screen which appears after activating the program.

5.4.2.2 Click the "Sample Information" button on the toolbar.

5.4.2.3 A blank sample information sheet appears. Previous sample information sheets may be obtained by activating the File - Open menu, designating "Sample Information" from the dialog which appears. The sample information sheet should be filled in to tell the computer which auto-sampler locations to go to.

5.4.2.4 Sample ID column - Some typing can be saved by double clicking on the column title. On the resulting form the job order may be typed in and the sample numbers will then be incremented by 1 for the autosampler locations indicated. The sample ID's will then be filled in. Sample: "9802094-0001..0002. .".

5.4.2.5 Sample weight column - For soil samples the weight of the samples should be filled in. At the top, the volume units should be filled in "mL", the weight units "g".

5.4.2.6 Sample units column - Typing may be saved by double clicking on the column title and indicating the units on the dialog box which appears, and indicating the AS locations involved. In the case of water samples this will ordinarily by "µg/L ". For soil samples the button "weight:weight" should be clicked and the desired units specified in the dialog box selected. If the dialog box has been properly filled in, the machine is programmed to compute the proper units (e.g. mg/kg). It should be kept in mind that this is on an as received basis, not a dry basis.

5.4.2.7 User dilution column - Where a dilution is involved (e.g. TCLP analyses) the dilution factor should be entered. As in the sample weight and sample units columns, above, typing may be saved by double clicking the column title.

5.4.2.8 The autosampler tray being used at present is "Tray B".

Sampler Location	Size	Contents
1	50 mL tube	Calibration Blank
2	50 mL tube	0.5 µg/L standard
3	50 mL tube	1.0 µg/L standard
4	50 mL tube	2.0 µg/L standard
5	50 mL tube	5.0 µg/L standard
6	50 mL tube	10.0 µg/L standard
7	50 mL tube	ICV
8	50 mL tube	ICB
9	15 mL tube	PBW or LCSS
10	15 mL tube	LFB or sample
11-109	15 mL tubes	Samples

5.4.3 All tubes should be marked with their contents before being filled. Then the tubes are filled from the BOD bottles and placed in the autosampler locations designated either by the method or by the sample information sheet.

5.4.4 At the beginning of each day of analysis, the following steps are taken to prepare the instrument:

5.4.4.1 The flows of the carrier solution and the reductant solution (the stannous chloride solution) are measured by the methodology suggested in the Perkin-Elmer handbook "Setting Up and Performing Analyses", 2.4.2-2.4.4. The rinse container (autosampler location 0) is rinsed and filled with 3% HCl solution. This is then analyzed using the location button in the analysis window of the automated analysis window, and the curve produced displayed through the curve button in the toolbar. The curve should be flat and less than 0.0001 absorbance units.

5.4.5 Analysis - The analysis is ordinarily started by clicking the "Analyze All" button in the Automated Analysis window. If only calibration is desired, the "Calibrate" button may be used. If samples are to be analyzed by an already existing calibration curve use the "Analyze Samples" button.

5.4.5.1 Once the analysis has been started the autosampler places the sampling probe in the sample/calibration cup. The peristaltic pump begins pulling sample through the sample loop. After the line has been purged, the injection valve cycles, and injects the sample into the carrier flow. This flow is then combined

with the SnCl2 and mixed. Next it goes to a liquid/vapor separator. The liquid goes to waste and the vapor is transported into the adsorption cell of the spectrophotometer. All samples and standards are measured in duplicate.

5.4.6 Run log - A run log will be printed as the analysis progresses. The print program is designed to transmit the data to be printed to the printer one page at a time. Thus several autosampler locations will be analyzed before anything appears on the printer. If anything else is printed (e.g. the sample information sheet) while the automated analysis window is open, the computer must be rebooted, or a run log will not be printed.

5.4.7 Additional samples may be analyzed after the run designated on the sample information sheet by using the "Select Location" button on the "Analyze" page of the Automated Analysis window. The autosampler locations should be filled in the resulting dialog.. The instrument will then analyze the samples indicated. This may be used to reanalyze the samples with questionable results, or to analyze diluted samples.

5.4.8 Dilution - Where analysis results are above the high standard (10.0 µg/L) an aliquot of the sample diluted with the calibration blank may be analyzed as set forth in 5.4.7 above.

6. Reports

6.1 Data Packet Organization

6.1.1 A report is prepared using the reformat procedure on the main menu. The reformatted design is entitled "Summary". It is transferred to a floppy disk, which is then imported to a spreadsheet using Microsoft Excel 5.0. This must then be formatted into the form included in Appendix III.

6.1.2 The final data packet is to include the following:

1) The report (See Appendix III).
2) The QC_DB Report Form
2) The digestion log (Appendix II).
4) The run log, if required.

6.1.3 All results for quality control tests are entered into QC_DB. A summary report of all data entered must be included in the data packet. The routine minimum is a method blank report, an MS/MSD or MS/duplicate report and a SRM/LSCW.

6.2 Data Qualifying Flags

Flag	Definition
U	The analyte of interest was not detected, to the limit of detection indicated.

6.3 Control charts

6.3.1 The recovery values for the LCS/SRM are plotted on control charts.

Appendix I - QC Summary Table

Laucks Testing Laboratories
Method 245.1,7471,7470 QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	CC > 0.995	CC > 0.995	once per batch	recalibrate	run log
Initial Calibration Verification	90-110 % SW846 80-120% 245.1	Per the method	one per 20	recalibrate	run log, report
Initial Calibration Blank	Below R.L.	Below R.L.	one per sequence	recalibrate	run log, report
Continuing Calibration Verification	80-120 %	80-120 %	At the beginning,every 10 samples and after the last sample	recalibrate and rerun samples since last CCV	run log
Continuing Calibration Blank	Below R.L.	Below R.L.	At the beginning,every 10 samples and after the last sample	recalibrate and rerun samples since last CCB	run log
Matrix Spike Recovery	SW-846 See QC_DB. CLP 75-125%	See QC_DB	Every 20 samples	Consult QC officer. Flag data or reanalyze.	QC_DB
MS/MSD RPD	See QC_DB	See QC_DB	Every 20 samples	Consult QC officer. Flag data or reanalyze.	QC_DB
Duplicate % Difference	20% RPD CLP	See QC_DB	Every 20 samples	Consult QC officer. Flag data or reanalyze.	QC_DB

Laboratory Fortified Blank (LFB)	85-115 %	See QC_DB	Once per 20	Recalibrate	Run log
Standard Reference Material (SRM) Recovery	Soil Manufacture's limits Water See ICV	Manufacturer's limits	Once per 20	Recalibrate	Run log

Appendix - II - Sample Digestion Log

Date		Bottles into water bath (time)	
Analyst		Water bath at 95°C (time)	
Standard ID	ME-	Bottles out of water bath (time)	
ICV No	ME-	Spike = 100 µl of Std	

No.	Sample ID	Sample size g , mL	Final volume,mL	Comments	Bottle #
	S0 ppb		100 ml		
	S0.2 ppb 20 µl of Std		100 ml		
	S0.5 ppb 50 µl of Std		100 ml		
	S1.0 ppb 100 µl of Std		100 ml		
	S2.0 ppb 200 µl of Std		100 ml		
	S5.0 ppb 500 µl of Std		100 ml		
	S10.0 ppb 1000 µl of Std		100 ml		
	ICV		100 ml		
	ICB		100 ml		
	LCSW		100 ml		
	CRA		100 ml		
	PBW		100 ml		
			100 ml		
			100 ml		
			100 ml		
			100 ml		
			100 ml		
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			100 ml		
			100 ml		
			100 ml		
			100 ml		

$NH_2OH \cdot HCl$	NaCl	$K_2S_2O_8$	$SnCl_2 \cdot 2H_2O$	$KMnO_4$
REA1-6-3	REA1-7-9	REA1-5-7	REA1-5-3	REA1-5-4

Appendix III - Example Report Form

Hg in Water and TCLP
Digested 1/7/98
Analyzed 1/8/98

Sample	Time	Value		% Rcvry	RPD	Flag	Comment
Calib Blank	11:13:29		µg/L				
S0.2	11:16:23		µg/L				
S0.5	11:19:19		µg/L				
S1.0	11:22:19		µg/L				
S2.5	11:25:17		µg/L				
S5.0	11:28:15		µg/L				
S10.0	11:31:16		µg/L				
ICV1 ME7-23-2=4	11:34:21	4.028	µg/L	101%			
ICB	11:37:21	0.001	µg/L				
CCV1=5	11:40:16	5.015	µg/L	100%			
CCB1	11:43:10	0.007	µg/L				
LCSW1	11:46:04	4.067	µg/L	102%			
CRA	11:48:57	0.226	µg/L				
PBW	11:51:55	0.003	µg/L				
12611-11	11:54:50	2.215	µg/L				did not report
12679-02	11:57:47	0.007	µg/L				
12679-02dup	12:00:44	0.017	µg/L				
12679-02ms Spk=1	12:03:42	12.842	µg/L	1284%		N	see below
12679-03	12:06:42	0.083	µg/L				
12679-04	12:09:34	-0.016	µg/L				
CCV2=5	12:12:28	5.138	µg/L	103%			
CCB2	12:15:24	0.013	µg/L				
12679-05	12:18:16	0.026	µg/L				
12679-06	12:21:11	0.029	µg/L				
12679-07	12:24:04	0.002	µg/L				
12679-08	12:26:58	8.239	µg/L				see below
12679-09	12:29:52	23.125	µg/L				did not report
12679-10	12:32:46	0.209	µg/L				did not report
12725-01	12:35:44	0.367	µg/L				
12725-02	12:38:39	-0.226	µg/L				
12725-02dup	12:41:36	-0.419	µg/L				
CCV3=5	12:44:32	4.945	µg/L	99%			
CCB3	12:47:26	0.014	µg/L				
12725-02ms Spk=200	12:50:25	199.903	µg/L	100%			
12184-5	12:53:22	1.436	µg/L				
12184-5dup	12:56:18	1.433	µg/L				
CCV4=5	12:59:16	5.111	µg/L	102%			
CCB4	13:02:10	-0.028	µg/L				
12679-02ms (rerun)	13:08:05	0.959	µg/L	96%			
12679-02ms (10x dil)	13:10:59	-0.646	µg/L				did not report
12679-08 (rerun)	13:13:49	0.001	µg/L				
12679-09 (10x dil)	13:16:40	0.211	µg/L				did not report
CCV5=5	13:19:35	4.940	µg/L	99%			
CCB5	13:22:32	0.011	µg/L				

Appendix IV - Example Sample Information Sheet

Autosampler Loading List

Sample Information File: 020598S.SIF
Methods: Soils

Location	Elements	Solution
0	Hg	Wash Solution
1	Hg	Calib Blank
	Hg	CCB1: 0.0000 µg/L
	Hg	CCB: 0.0000 µg/L
2	Hg	S0.2: 0.2 µg/L
3	Hg	S0.5: 0.5 µg/L
4	Hg	S1.0: 1.0 µg/L
5	Hg	S2.0: 2.0 µg/L
6	Hg	S5.0: 5.0 µg/L
	Hg	CCV1: 5.0000 µg/L
	Hg	CCV: 5.0000 µg/L
7	Hg	S10.0: 10.0 µg/L
8	Hg	ICV: 4.0000 µg/L
9	Hg	ICB: 0.0000 µg/L
10	Hg	Sample: CRA
11	Hg	Sample: PBW
12	Hg	Sample: LCSS
13	Hg	Sample: 9801614-01
14	Hg	Sample: 614-01ms
15	Hg	Sample: 614-01msd
16	Hg	Sample: 549-02 (10x)
17	Hg	Sample: 549-03 (10x)
18	Hg	Sample: 549-03(20x)

LAUCKS TESTING LABORATORIES INC.

Seattle, Washington

SOP #:LTL-8000

Title: **Determination of Retention Time Windows**

Revision history:

Number	Date
0	10/30/94
1	1/30/98

Written by: _____ Date: 2/2/98

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1. Introduction and Scope

1.1. Method Description

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for compound identification in all GC, HPLC, and ion chromatographic determinations. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of normal chromatographic variability.

The width of the retention time windows should be such that the occurrence of both false positives and false negatives is minimized. Retention time windows that are too narrow can result in false negatives or may cause unnecessary reanalysis of sample extracts when surrogate or matrix spike compounds cannot be correctly identified. Conversely, retention time windows that are too wide may result in false positive results that cannot be confirmed by secondary column analysis, or other methods.

This procedure describes the methodology used to establish retention time windows for chromatographic methods. It is based on the practice outlined in SW846, Method 8000. In general terms, standards are analyzed over a time period of no less than 72 hours. Injections made over a period of less than 72 hours may result in retention time windows that are unrealistically small.

The measured retention times of the standards are tabulated and a statistical measure of retention time stability is computed. This measure is then used to set the retention time window half-width used for analyte identification.

In general, a retention time window study is performed during method validation. The retention time windows thus determined are subsequently used for analyte identification during sample analysis. This method is intended to apply to all chromatographic methods performed at Laucks that do not employ a mass spectrometer as the detector: gas chromatography, HPLC, and ion chromatography.

2. Definition of terms and acronyms

2.1. RTW (Retention Time Window)

The width, in minutes, of the retention time window half width. The retention time window for identification is ±RTW.

3. Equipment list and standards

3.1. Equipment

3.1.1. Chromatographic system

The same system that will be used for the analysis of samples or sample extracts. Ensure that the chromatographic system is operating reliably and that conditions have been optimized for the target analytes and surrogate compounds to be determined in the method.

3.2. Standards

Calibration standards required by the method.

4. Safety precautions and waste disposal

4.1. Safety precautions

4.1.1. Standards, samples, and samplesolutions

Handle as if they are hazardous substances.

4.1.2. Instrument operation

Refer to the instrument manufacturer's manual for routine instrument precautions.

Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

4.1.3. Electrical shock

All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

4.2. Waste disposal

4.2.1. All waste disposal precautions and procedures will be detailed in the appropriate analysis SOP.

4.2.2. Waste segregation and disposal from the point of collection is further covered in the appropriate Laucks SOP.

5. Calibration and quality control

5.1. Calibration

Calibrate the instrument as described in the analysis SOP. Before establishing windows, make sure that the chromatographic system is operating under optimal conditions.

6. Operation procedures

6.1. Data collection

For the data collected over the course of at least one analytical sequence no less than 72 hours long, tabulate the analyte retention times for all method target analytes and surrogate compounds from all standards analyzed.

> **Note**
>
> A single analytical sequence is the minimum requirement. In most cases it is advisable to collect data over additional sequences in order to capture a data set of retention times which more closely models real world operating conditions.

To mimic real world operating conditions the standards must bracket sample extracts just as in a normal sample analysis sequence. Collect data for a minimum of 3 standards in each sequence. For multi-response analytes such as Aroclors, select the same peaks which will be used for compound identification.

Record the retention time for each single component target analyte, surrogate spiking compound, and multi-component representative peak to 3 decimal places.

6.2. Calculations

Compute the mean and standard deviation of the measured retention times for each compound using the following equations.

6.2.1. Mean

$$\bar{t} = \frac{\sum_{1}^{n} t_i}{n}$$

6.2.2. Standard deviation

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(t_i - \bar{t}\right)^2}{n - 1}}$$

where

t_i=measured retention time

$\bar{t}$ =average retention time

n=number of measurements

6.2.3. Retention time window

$$\text{RTW} = \bar{t} \pm 3 * SD$$

6.2.4. Frequency of RTW determination

This study must be repeated whenever there is a major change to the method such as a new column, a new instrument temperature program, a new gradient program, major instrument overhaul, etc. It is desirable that multiple instruments running the same method have identical RTWs. However, this must be verified experimentally.

6.2.5. Constraints on the experimental determination of RTWs

6.2.5.1. RTW too small

In spite of the effort to mimic real world operating conditions by performing this study using a real analytical sequence, the RTWs may be unrealistically small, even 0.000 minutes, to the limits of the chromatography system. In that case use one of the following methodologies to administratively set the RTWs. When applying one of the administrative methodologies, the analyst's judgment weighs heavily. The desired result is that the RTWs be set such that the window half-width is sufficient to ensure that the chance for both false negatives and false positives is minimized.

6.2.5.1.1. Method 1

Collect additional data and re-compute the RTWs.

Note:

Collecting data over more than one 72-hour analytical sequence should preclude a necessity to use Method 1.

6.2.5.1.2.Method 2

Set the RTW using the following guidelines.

Run Type	RTW half-width, minutes
Narrow bore, megabore capillary	0.03
HPLC	0.15 for analytes with RT to 15 min, 0.20 thereafter (see following notes)
Ion chromatography	0.15 for analytes with RT to 15 min, 0.20 thereafter (see following notes)

Notes:

In the determination of pesticides/PCBs using CLP methodology, the RTWs are fixed in the Statement of Work. This methodology will not apply to pesticides/PCBs determined using the CLP SOW.

The default retention time window half-width (0.03 minutes) that is called out in SW-846 is unrealistically small for HPLC determinations. The numbers listed in the table above are based on Laucks experience with these methods. In most cases, there will be sufficient retention time variation for HPLC analytes that this option will not be necessary.

This method is also implemented for ion chromatography. Ion chromatography is not addressed in SW-846, method 8000.

6.2.5.2. RTW too large

IF, in the analyst's judgment, the compound RTW is too large THEN compute a pooled standard deviation using the following equation. Using this pooled estimate, re-compute the RTW as ±3 times the pooled estimate.

$$s_{pooled} = \sqrt{\frac{\sum_{1}^{k} s_k^2 (n_k - 1)}{\sum_{1}^{k} (n_k - 1)}}$$

k=k*th* set

s_k^2 =variance of k*th* set

n_k =replicates in k*th set*

7. Application to routine analytical sequences

7.1. Setting the RTW for each analytical sequence

The analytical method for each SOP covers this in more detail, but the general methodology is as follows. After the analysis of either the initial multi-point calibration standards or the analysis of the initial calibration verification standard, the RTWs for analyte identification in that analytical sequence are reset using the retention times of the mid-point calibration standard as the center of the window.

7.2. Analyst discretion in analyte identification

Irrespective of the RTW established for analyte identification, the judgment of the analyst weighs heavily in the interpretation of chromatograms. Sample-specific effects can alter the observed retention times of target analytes in sample extracts. In such

cases, it is acceptable for the analyst to determine that the target analytes are outside the established RTWs.

Some techniques that are used for such identifications are retention time ratios of target analytes to surrogate compounds, observation of retention times of target analytes in MS/MSD samples, or re-analysis of sample extracts after spiking the extract with target analytes and observing an increase in peak response. Whatever methodology is used must be completely documented in narrative comments for the sample set.

7.3. Corrective actions

The surrogate compounds added to each sample, blank, QC sample, and calibration standards are used to monitor retention time shifts. IF a surrogate compound's retention time falls outside the expected RTW THEN the analyst must determine the cause and correct the problem before proceeding with further determinations.

Note

In some cases sample-specific matrix effects may result in uncorrectable retention time shifts of surrogate compounds. These effects must be documented on a sample by sample basis and the corrective action used for compound identification documented.

The retention times for all target analytes in continuing calibration standards must fall within the established windows. IF retention times drift outside the established windows THEN perform instrument maintenance, analyze a new initial calibration verification standard, and reset the RTW centers.

8. Reports

8.1. Original data

The appropriate analytical department will retain the original files of all RTW studies.

8.2. Working copies

Summarized, tabulated retention time window results will be maintained in the appropriate chromatography laboratory, on an instrument specific basis. On a project specific basis and by request only, these summarized, tabulated RTW results will be provided in the case narrative report.

In addition, these retention time window study summaries will be signed off by the department manager and the summary report scanned and stored in LaserFiche.

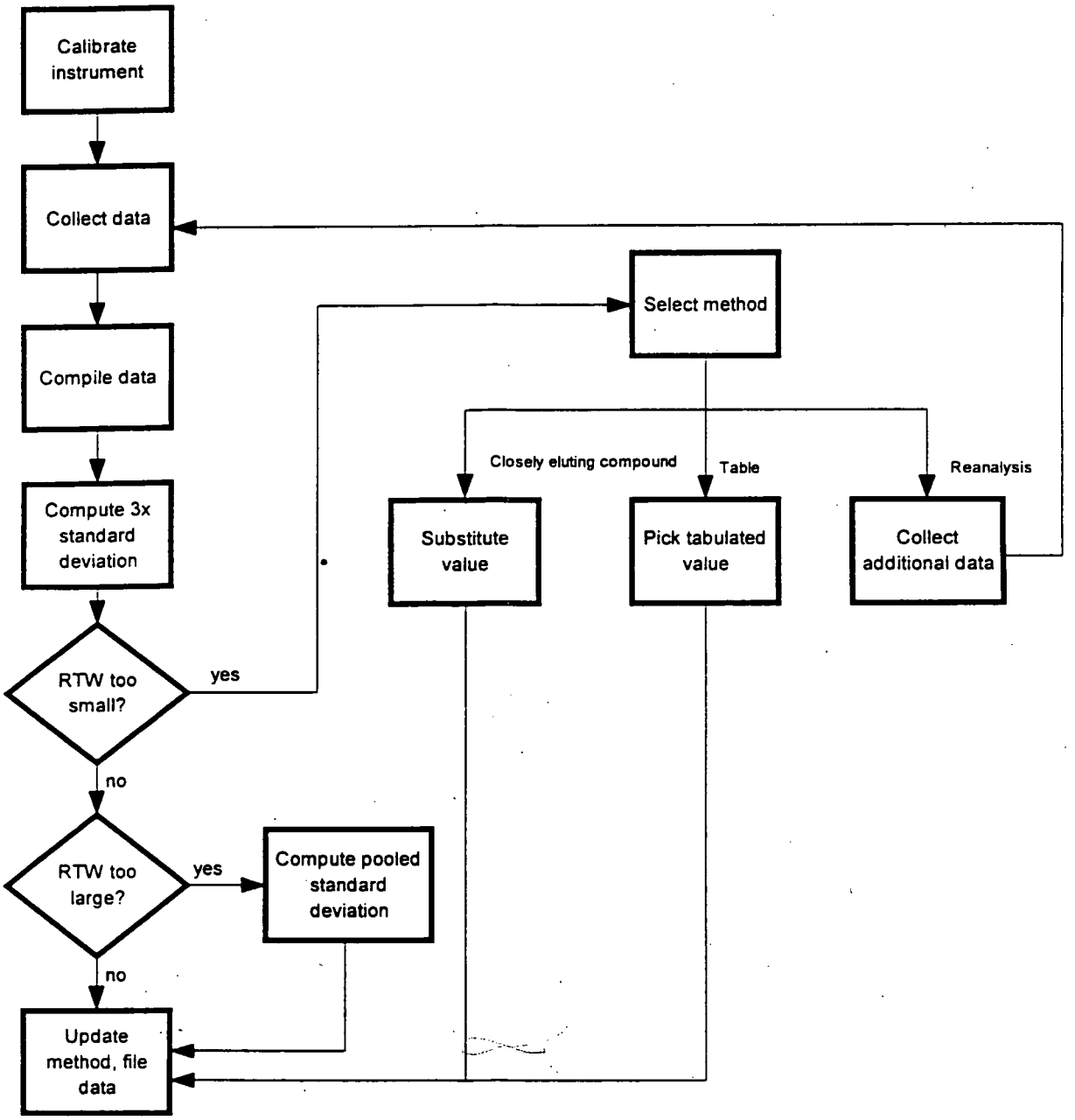
References:

John Keenan Taylor, *Quality Assurance of Chemical Measurements*, Lewis Publishers, 1989

USEPA, *Test Methods for Evaluating Solid Waste*, SW-846, 8000B, various analytical methods.

9. Appendix 1, Flow Chart

Method LTL-8000



LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8019

Determination of Non-Halogenated Volatile Organics by SW 8015B

Revision history:

Number	Date
0	10/08/97
1	01/16/98
2	04/22/98
3	12/09/98

UNCONTROLLED

Revised by: Monica Carr, Organics Division Manager Date: 12/9/98

Approved by: Harry Romberg, QA Officer Date: 12-9-98

Approved by: Kathy Kreps, Laboratory Director Date: 12-9-98

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1. Introduction and Scope

1.1 Method Description

Method 8015B is used in the determination of nonhalogenated volatile organic compounds and semivolatile organic compounds by gas chromatography. 8015B may also be applicable for the analysis of petroleum hydrocarbons, including gasoline range organics (GROs) and diesel range organics (DROs). However, this SOP is written strictly for the determination of nonhalogenated volatile organic compounds in soil, sediment, aqueous, and other matrices. This method employs sample introduction via a purge and trap sample concentrator.

A tabulated list of Laucks' typical analytes is located in Appendix I. The actual target analyte list may vary, depending on project specific requirements. This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatography and in the interpretation of chromatograms. Each analyst performing this method must have demonstrated the ability to perform the described chromatographic analysis and/or data interpretation.

1.2 Decision-making Process

In order to attain lab-wide consistency among staff members for decision-making processes with regard to laboratory anomalies, several common items have been addressed in this SOP. Any occurrences which are not covered in this SOP should be discussed with the supervisor, prior to implementing a solution.

One example is the determination of potential carry-over in sample analyses. Any samples analyzed subsequent to a high level sample (which is defined by yielding one or more target analytes above the calibration range) should be thoroughly examined for potential carry-over of the same target analyte(s). Corrective action in the form of reanalysis for possible carry-over should be performed and documented in the narrative.

Another example is the review of all sample chromatograms for analytes which may not show up on the sample quantitation report due to data system error or retention time shift. All peaks should be examined and evaluated based on the retention times and sample concentration in order to prevent reporting false negatives.

1.3 Sample Collection, Sample Storage, Holding Times

1.3.1 Waters

1.3.1.1 Samples are collected with zero headspace in 40 mL glass containers containing preservative (HCl) and sealed with Teflon-lined caps. The water samples are preserved to a pH of ≤2, and all samples are stored at 4°C.

1.3.1.2 The holding time to analysis is 14 days from date of collection. The pH values for the water samples are measured at the time of sample preparation. The pH values, when not preserved to a pH ≤2 are noted in the instrument logbook and the client report.

1.3.2 Soils

1.3.2.1 At the time of this writing, the 3rd update of the 3rd edition to SW 846 requires that low level soils be collected in duplicate using 5 gram and/or 1 gram aliquots which are to be weighed out in the field. The soil samples are to be collected in a 40 mL vial containing water, sodium bisulfate, and a stir bar. 0.2 grams of sodium bisulfate are added for each 1 gram of soil. Therefore, when collecting 5 grams of sample, the VOA vial should contain 1 gram of sodium bisulfate. The sodium bisulfate is added in order to ensure a sample pH of ≤2. The vials used for low level soils should have the tared weight recorded on the label and sealed with septum-lined screw caps.

1.3.2.2 Laucks' prefers to use the other option, which is the use of the EnCore™ sampler, the Purge-and-Trap Sampler™, or a cut plastic syringe to transfer the sample to the soil vial. If the EnCore™ sampler is used in the field, the samples may be stored for up to 48 hours. However, samples collected in this device should be transferred to the soil sample vials (and preserved) as soon as possible, or analyzed within 48 hours. The holding time for soils is 14 days from the date of collection.

1.3.2.3 At the time of this writing, the 3rd update of the 3rd edition to SW 846 requires that high level soils be collected in using one of the following options:

1.3.2.3.1 Option 1: Samples will be collected in duplicate using 5 gram and/or 1 gram aliquots which are to be weighed out in the field. The soil samples are to be collected in a 40 mL vial containing methanol. The vials used for high level soils should have the tared weight recorded on the label and sealed with septum-lined screw caps.

1.3.2.3.2 Option 2: Samples will be collected using an EnCore type sampler or equivalent, and preserved at the laboratory.

1.3.2.3.3 Option 3: Samples will be collected in vials with zero headspace.

1.3.2.4 The practices in sections 1.3.2.1 and 1.3.2.2 will be implemented as SAPs, QAPs, agencies and clients require without updating this SOP until the practice is routine and this document is up for its annual review. Until this practice is routine and accepted by all agencies Laucks will continue to accept unpreserved soil samples for low or high level analysis. The samples must be collected in 2- or 4-oz glass containers and sealed with teflon-lined caps. These samples will be introduced by method 5030A and analyzed according to this SOP.

1.3.2.5 The holding time to analysis is 14 days from date of collection.

1.4 Definition of Terms

This section defines terms and acronyms as they are used in this SOP. Not all of the terms are defined here since it is assumed that the user of this SOP already understands their general meaning.

Method Blank Spike	A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts or target analytes and surrogates are added each time sample extracts are prepared. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard. A blank spike is analyzed at a rate of 5% per matrix per day.
CCV	Continuing calibration verification. This is a standard injected at some prescribed frequency during the analysis sequence to determine whether the instrument has remained in calibration.
ICV	Initial calibration verification. The ICV is used in the same capacity as a CCV to check for continuation of the calibration, however, this standard is also used to adjust the mid-point of the retention time window on extended QC periods. Calibration is set by the initial multi-point curve.
CF	Calibration factor. The ratio of peak response to nanograms injected.

Corr Coef, r	Correlation coefficient. A measure of the "goodness of fit" of a set of data to a linear regression model. The closer the value is to 1, the higher the degree of confidence in the correlation. The correlation coefficient must be greater than 0.990 to be acceptable. (Specific projects may require a greater degree of confidence by using a correlation coefficient of 0.995.)
DIW	Deionized water. Lab reagent water. Organic-free water. Since the systems used to provide DIW at Laucks all contain carbon polishing filters, they are capable of providing organic-free water for use in method blanks and method blank spikes.
IBLK	Instrument blank. An instrument blank contains the method surrogates and is injected into the instrument to monitor for carry over between sample extract injections.
IDL	Instrument detection limit. The lowest concentration of a target analyte that will yield a signal:noise ratio of at least 3x. Used as a starting point for selecting MDL study spiking levels.
MDL	Method detection limit. The lowest concentration in a sample which will yield a positive result that is greater than zero at a known level of confidence. MDLs are empirically determined by Laucks.
Method Blank	Surrogate is added to purge-free water. The purpose of the method blank is to demonstrate that interferences from the analytical system, glassware, laboratory contamination, and reagents are within tolerance. A method blank is analyzed at a rate of 5% per matrix per day.
MS/MSD	Matrix spike and matrix spike duplicate. A known amount of the target analytes and surrogates are added to a sample at a rate of 5% per matrix (1 MS/MSD set per 20 sample matrices).
PFW	Purge-free water. Deionized water that has either been purged with high purity nitrogen for 15 minutes at 10 psi or has been boiled for 45 minutes in an environment free of all purgeable organics, cooled and sealed for later use.

QC Check Standard	Quality control check standard. Referred to in this SOP as a blank spike. A QC check standard is a requirement of SW 846 method 8000 and is used to determine whether the analytical system is in control if MS/MSD recoveries are out of control. See also blank spike.
QC Period	Quality control period. An analysis sequence initiated by the injection of one or more standards, followed by sample extracts, and terminated with a standard injection. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP.
RF	Response factor. The ratio of nanograms injected to peak response. This term is defined in the same way in both the CLP contract and SW 846.
RSD or %RSD	Relative standard deviation or percent relative standard deviation. The ratio of the standard deviation of a set of values to the mean of the set of values. A measure of the similarity of the values one to another.
RT	Retention time. The time (in minutes) at which a target analyte elutes from the GC column.
RT Window	Retention time window. The +/- value which is applied to the ICV to establish the time range used to make tentative compound identifications.
Sequence	A set of samples and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.

2. Equipment List and Standards

2.1 Chromatographic System

Gas Chromatograph:	Hewlett Packard, 5890 or equivalent.
Data System:	EZChrom data acquisition system, revision 6.6, Target/NT data processing system, revision 3.21 capable of off-line data storage or equivalent.
Detectors:	Dual FID detectors from Hewlett Packard or equivalent.
Purge and trap:	Tekmar LSC 2 or equivalent.
Autosampler:	Dynatech PTA-30W/S, Tekmar ALS 10 or equivalent.
Trap:	Tenax/OV1 (Supelco G Trap). Other packings for the trap may be substituted if equivalent or improved performance can be demonstrated.
Columns:	1) 30m x 0.53mm x 3.0 film bonded phase fused silica capillary (DB-624). 2) 30m x 0.45mm x 3.0 film bonded phase fused silica capillary (DB-VRX).

2.2 Supplies and Materials

Syringes:	10 and 25 mL Luerlok syringes.
Microsyringes:	10 and 25 µL syringes with a 0.006 in. I.D. needle (Hamilton 702N or equivalent) in addition to 50, 100, 500 and a 1000 µL gas-tight syringes.
Volumetric flask:	Class "A" type volumetric flasks of assorted volumes ranging from 10 to 100 mLs.
Micro reaction vials:	1 and 2 mL micro reaction vials with Mininert valves for storing current standard solutions.
VOA vials:	20 mL VOA vial with Teflon-lined caps.

Compressed gases:	Hydrogen 99.995% (high purity) or better. Helium 99.995% (high purity) or better. Air (breathing air grade without trace hydrocarbons) or purified air from the Balston 75-80 Zero Air Generator.
Reagent water:	Reagent water also known as purge-free water is deionized water that has been boiled for 45 minutes in an environment free of purgeable organics.
Methanol:	B&J Purge and Trap quality or equivalent.
Disposable pipettes:	1, 5, and 10 mL disposable pipettes.
Stainless steel spatula.	
Analytical balance:	Capable of accurately weighing to the nearest 0.0001 gm for standard preparation and a top loading balance capable of weighing to the nearest 0.01 gm for samples.
Note:	All of the above equipment may be substituted with equivalent or better equipment.

2.3 Standards

2.3.1 Preparation of Standards

Standards - Some of the standards are prepared from neat chemicals, but many of the compounds are purchased as pre-mixed multi-component standards.

The Neat/Standard book is used for creating a discrete entry for each standard. The information entered into the book documents the traceability of all standards that are used (i.e., source, lot number, purity, date made, expiration date). In addition all standards are labeled with the standard concentration, the solvent, date prepared, expiration date, analyst's initials, and the standard reference number.

Quality control is maintained on all solutions by verifying the standard solutions prior to use. This is accomplished through analysis of the new solution against a current 5-point calibration. Analyte values within 80-120 percent of their nominal value are considered acceptable.

Spiking solutions for the blank spikes and MS/MSD analyses are prepared in the same manner as the calibration standards. To verify the integrity of working calibration standards, a second source or discrete lot number is used for the QC standards.

All stock standards are stored at -10°C in flame-sealed amber ampules for a time period not to exceed six months or the expiration date of the parent standard. However, due to their volatility, the gases are stored for a time period not to exceed 2 months.

Standards are removed from the freezer and allowed to warm to room temperature prior to use.

When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at the concentration that the manufacturer guarantees if they are certified by the manufacturer or by an independent source.

2.3.2 Preparation of Surrogate Standards

If starting with a neat material, a measured amount of the neat chemical is placed in a glass volumetric and filled to the mark with it's appropriate solvent, then stoppered. A common dilution is approximately 125 mg of neat material into 25 mL of methanol. This yields an intermediate solution of 5000 ng/µL. This solution is stored in flame-sealed amber ampules for a time period not to exceed one year or the expiration date of the parent standard.

Surrogates	Source*	Concentration
Bromofluorobenzene	Supelco	5000 ng/µL
Trifluorotoluene	Supelco	5000 ng/µL

* or equivalent.

Aliquots of the 5000 ng/µL stock solutions are taken from the surrogate standards and then combined in a volumetric flask and diluted with methanol to yield a working level multi-component standard of 20 ng/µL. This solution is stored in flame-sealed amber ampules for a time period not to exceed six months or the expiration date of the parent standard, whichever is sooner.

Surrogate	Conc.	Aliquot	Vol.	Conc.
Bromofluorobenzene	5000 ng/µL	40 µL	10 mL	20 ng/µL
Trifluorotoluene	5000 ng/µL	40 µL	10 mL	20 ng/µL

Below is the surrogate concentrations and the preparation for sample analysis.

Surrogate	Conc.	Aliquot	Vol.	Conc.
Bromofluorobenzene	20 ng/µL	10 µL	10 mL	20 µg/L
Trifluorotoluene	20 ng/µL	10 µL	10 mL	20 µg/L

2.3.3 Preparation of Matrix Spike Standards

Certified solutions of each of the spiking compounds are received at concentrations of 2000 ng/µL. Isobutyl alcohol, acetonitrile, and propionitrile are diluted in methanol to working concentrations of 200 ng/µL. The working solutions are stored in Mininert vials for an extended period of time not to exceed six months or the expiration date of the parent standard, whichever is sooner.

Matrix Spike Solution	Source*	Concentration
Isobutyl alcohol	Accustandard	2000 ng/µL
Acetonitrile	Accustandard	2000 ng/µL
Propionitrile	Accustandard	2000 ng/µL
1,4-Dioxane	Supelco	2000 ng/µL

* or equivalent.

Matrix Spike Solution	Conc.	Aliquot	Vol.	Conc.
Isobutyl alcohol	2000 ng/µL	100 µL	1 mL	200 ng/µL
Acetonitrile	2000 ng/µL	100 µL	1 mL	200 ng/µL
Propionitrile	2000 ng/µL	100 µL	1 mL	200 ng/µL
1,4-Dioxane	2000 ng/µL	NA	NA	2000 ng/µL

Below are the spike concentrations and the preparation for the blank spike and MS/MD analyses.

Matrix Spike Solution	Conc.	Aliquot	Vol.	Conc.
Isobutyl alcohol	200 ng/µL	5 µL	10 mL	100 ng/mL
Acetonitrile	200 ng/µL	5 µL	10 mL	100 ng/mL
Propionitrile	200 ng/µL	5 µL	10 mL	100 ng/mL
1,4-Dioxane	2000 ng/µL	5 µL	10 mL	1000 ng/mL

2.3.4 Preparation of Initial Calibration Standards

Certified sets of working solutions which contain the target analytes are purchased pre-mixed from a commercial supplier at a concentration of 2000 ng/µL (100 ng/µL for 1,4-dioxane). If additional target analytes are requested, these analytes may be ordered separately; in solution or as a neat material and diluted to appropriate working concentrations through the above described methods.

These solutions are then diluted in methanol to generate working standards at concentrations of 200 ng/µL and 100 ng/µL. These solutions are stored in flame-sealed amber ampules for a period of time not to exceed six months or the expiration date of the parent standard, whichever is sooner.

The working standards contain the following compounds in each solution:

Analytes	Working Solution
Isobutyl alcohol	Mix 1
Propionitrile	Mix 1
Acetonitrile	Mix 1
1,4-Dioxane	Mix 3
Surrogates	
Trifluorotoluene	Mix 2
Bromofluorobenzene	Mix 2 and Mix 4

Standards are kept in the VOA freezer at -10°C to -20°C and removed prior to making up the initial calibration standards and are allowed to warm to room temperature.

The initial calibration standards range from 40 µg/L to 300 µg/L for the non-dioxane compounds and 100 µg/L to 3000 µg/L for 1,4-dioxane . The standards are prepared by withdrawing aliquots of the working solutions and injecting them into a 10 mL syringe containing P.F.W. The surrogate solution is then added to the syringe.

Working Solution Conc. (non-dioxane cmpds)	Aliquot	Final Volume	Concentration
200 ng/µL	2 µL	10 mL	40 µg/L
200 ng/µL	4 µL	10 mL	80 µg/L
200 ng/µL	5 µL	10 mL	100 µg/L
200 ng/µL	10 µL	10 mL	200 µg/L
200 ng/µL	15 µL	10 mL	300 µg/L

Surrogates	Aliquot	Final Volume	Concentration
20 ng/µL	2 µL	10 mL	4 µg/L
20 ng/µL	5 µL	10 mL	10 µg/L
20 ng/µL	10 µL	10 mL	20 µg/L
20 ng/µL	15 µL	10 mL	30 µg/L
20 ng/µL	20 µL	10 mL	40 µg/L

Working Solution Conc. (1,4-Dioxane)	Aliquot	Final Volume	Concentration
100 ng/µL	10 µL	10 mL	100 µg/L
100 ng/µL	50 µL	10 mL	500 µg/L
100 ng/µL	100 µL	10 mL	1000 µg/L
100 ng/µL	200 µL	10 mL	2000 µg/L
100 ng/µL	300 µL	10 mL	3000 µg/L

2.3.5 Preparation of a Continuing Calibration Standard

The concentration of the continuing calibration standard is the mid-point of the initial calibration curve. Due to its volatility, this solution is not stored for any period of time.

3. Safety precautions

3.1 Routine Safety Precautions

Many analytes in this method are known or suspected carcinogens. Analysts should handle all neat materials, standards, and samples as if they were potentially hazardous substances. Respirators and fume hoods should be employed for extremely hazardous materials.

Refer to the instrument manufacturer's manual for routine instrument precautions.

Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

Methanol should be stored in a solvent locker and kept away from sources of heat and sparks. Contact should be avoided.

3.2 Waste disposal

All expired standards are discarded in the solvent waste container located in the prep area under the fume hood.

All high level samples are either returned to the client for disposal or are disposed of in the appropriate waste container.

Soil samples are dumped into a 55 gallon drum in the warehouse where an outside source disposes of the waste.

4. Operation procedures

4.1 Analytical Conditions

4.1.1 Chromatographic Conditions

Initial GC Temperature :	40°C
Hold Time :	3.0 min.
Ramp Rate:	8°C/min.
Final Temperature:	200°C
Final Time:	3 min.
Carrier Gas Flow:	10 mL/min.

4.1.2 Purge & Trap Parameters

Purge Time:	11 min.
Desorb Time:	4 min.
Bake Time:	15 min.
Desorb Preheat Temperature:	160°C
Desorb Temperature:	160°C
Purge Flow:	40 mL/min.
Purge Temperature:	40°C
Bake Temperature:	180°C
Desorb Flow Rate:	10 mL/min.

Dynatech Autosampler

Selection	Selected	Choice	Comments
Program set up	Auto	Man	Select Auto by using the arrow
Start Delay	0.0		
Cycle Time	30		May vary depending on the GC
Aux Output	0		
Last Water	0		NEVER select anything but 0
Last Soil	1-30		Set according to # of samples
Blank Last	No		
Flush Vol.	5 mL		
Purge Setup	Soil	Water	Select Soil by using the up arrow
Standard	No		
Flow Rate	40 cc		
Line Heat	110C		
Sample Heat	25C		
Pre-Heat	0.0 min.		
Water Vol.	0.0 mL		
Pre-purge	0.0 min.		
Purge Time	12 min.		
Flushes	0		
Soil Stir	No		
Desorb Time	4 min.		
Water Trap Vol.	0		
Purge Setup	Soil	Water	System is verifying Setup, ENTER
Program set up	Auto	Man	System is ready, to start, AUTO

4.2 Method Detection Limit Study

Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in the Laucks SOP for MDL determinations. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration near the anticipated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL.

4.3 Method Validation

Prior to the analysis of any samples, it is necessary to validate the method. A method validation study is performed in a similar manner to an MDL study with the exception that a minimum of 4 replicates are required and the concentration levels are typically 10-50 times the MDL. In the absence of criteria for the initial demonstration of proficiency, the limits of 70%- 130% can be used.

4.4 Method Reporting Limits

Method reporting limits are based on the low level calibration standard, in accordance with SW 846.

4.5 Retention Time Windows

Prior to the analysis of any samples, it is necessary to establish retention times windows for the method by analyzing standards for all target analytes over at least a 72-hour period. These standards should be inter-mixed with real sample extracts in order to mimic actual instrument operating conditions. Tabulate the retention times for all standard compounds and compute the standard deviations of all the retention times.

The retention time window half-width is set at 3 times the above calculated standard deviation. This operation must be repeated whenever major equipment changes are made or whenever the chromatographic method is modified.

In some cases, particularly for narrow bore capillary column analyses, the calculated retention time window half widths may be an unrealistically small value or even zero. If that is the case then substitute a retention time window of a close eluting, similar compound to develop a valid retention time window.

4.6 Initial Multi-Point Calibration

Analyze standard solutions using a minimum of 5 different concentration levels. The lowest concentration should define the reporting limit. The highest concentration should define the upper usable working range of the detector. Evaluation criteria are detailed in Section VI. Refer to Appendix II for a tabulated list of calibration standard concentrations.

4.7 Initial Calibration Verification

Prior to sample analysis a mid-range calibration standard analysis is performed. The computed calibration factor (CF) must meet the criteria detailed in Section VI.

The retention time windows for compound identification are updated using the retention times for each target analyte in the ICV standard as the center of the window and the previously determined retention time window half-width to establish the retention time range to be used for compound identification.

4.8 Continuing Calibration Verification

A mid-range calibration standard is analyzed at the frequency of no more than ten injections between CCVs. All injections, whether they are instrument blanks, blank spikes, or dry purges, are considered samples. In addition, this standard must be the last injection made in the analysis sequence. Evaluation criteria are detailed in Section VI.

4.9 Sample Analysis

The ICV criteria and method blank criteria must be met prior to analyzing samples.

4.9.1 Analysis sequence

See Appendix III for a detailed sample analysis sequence.

4.9.2 Sample Preparation

The samples are removed from the VOA refrigerator and are allowed to warm to room temperature.

4.9.3 Water Sample Preparation

A 10 mL aliquot of the water sample is transferred to a 10 mL syringe, where 10 µL of the surrogate solution is added. The sample containing the surrogate solution is then transferred to a VOA vial and loaded onto the autosampler. The sample volume is recorded in the instrument logbook. The remaining sample is transferred into a 20 mL VOA vial with zero headspace and sealed with a Teflon-lined cap.

If samples require a dilution then a sample aliquot is transferred to a 10 mL syringe.

4.9.4 Soil Sample Preparation

The sample consists of the entire contents of the sample container. Do not decant any of the supernatant liquids. All soil samples must be stirred gently, before removing an aliquot.

4.9.5 Low Level Soils

1.0 grams of soil are weighed in a VOA vial, or the entire contents from the EnCore sampler is used. The actual sample weight should be recorded, instead of rounding to the nearest gram. For example, 0.95 and 1.05 grams should be recorded as 1.0 gram, not 1 gram.

10 mls of reagent water containing the surrogate solution are transferred to the vial containing the soil sample. Refer to the water preparation above for details on the surrogate amount.

4.9.6 Medium Level Soils

Weigh 5.0 grams of soil (recorded to the nearest 0.1 gram) into a VOA vial, add 0.1 mL of surrogate solution to the sample and add 9.9 mL of methanol to the vial. Shake the sample for 2 minutes and let the suspended solids settle before use. Transfer 100 µL of the aliquot to 10 mL of PFW. Record the sample weight and the aliquot amount in the instrument logbook.

The same GC conditions apply to soil samples as water samples, except that the temperature during the purge cycle must be set to 40C.

4.9.7 Dilution Criteria

All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the calibration.

4.9.8 Compound Identification

Compounds are tentatively identified if a peak elutes in the retention time window characteristic of that compound on the primary column. To confirm the presence of that compound in the sample extract, the peak must also elute in its retention time window on a second column. Retention time windows are established as previously described and are updated each QC period. Compounds can only be identified if the ICV and CCV criteria detailed in Section VI are strictly adhered to.

The experienced analyst's judgment weighs heavily in evaluating chromatograms for compound identification. For instance as referenced in Part 2, Decision-making Process, the retention times of analytes and surrogates may be outside their expected windows due to sample matrix effects. The analyst may decide to re-adjust the target analyte's retention time windows on an ad hoc basis based on such an observed shift. If this is done, it must be fully documented in the case narrative notes.

4.9.9 Compound Quantification

Target compound concentrations are calculated using the external standard calibration equations.

4.9.9.1 Aqueous samples

As expressed in SW846 is:

$$Concentration(\mu g / L) = \frac{As \times Vt \times D}{\overline{CF} \times Vi \times Vs}$$

where:

V_t = Total volume of the concentrated extract (µL). For purge-and-trap analysis, V_t is not applicable, and therefore is set at 1.

A_s = Area or height of the peak for the analyte in the sample.

V_i = Volume of extract injected, µL. For low level purge and trap analysis, $V_i = 1$. For medium level purge and trap analysis there is a term for Vi.

D = Dilution factor of extract. The final result of an algebraic multiplication of the ratio of all dilution final volumes to initial volumes. For example, if a high level sample was diluted 100 µL to 10000 µL and subsequently diluted an additional 100 µL to 10000 µL, the expression would be: (10000/100) * (10000/100) = 100 * 100 = 10,000. If no dilution was made, D = 1.

V_s = Volume of the aqueous sample extract or purged in 1 mL. If units of liters are used for this term, multiply the results by 1000.

4.9.9.2 Non-aqueous samples

The results calculation for non-aqueous samples is very similar to that for aqueous samples. The only difference is the inclusion of a total solids term to calculate the dry weight equivalent of the initial sample size.

$$Concentration(\mu g / kg) = \frac{As \times Vt \times D}{\overline{CF} \times Vi \times Ws}$$

where:

W_s = Weight of sample extracted or purged, in grams. Either the wet weight or dry weight may by used.

V_t, D, A_s, and V_i have the same definition as for aqueous samples when a solid sample is purged. When a non-aqueous sample is extracted for purge and trap analysis, V_i = volume of methanol extract added to reagent water for analysis.

5. Reports

5.1 Data Packet Organization

See Appendix IV for a check list detailing data packet organization.

5.2 Quality Control Reports

All results for quality control tests are entered into the lab QC database. Printouts of all data entered must be included in the data packet. The routine minimum is a method blank report, a method blank spike report, and an MS/MSD report.

5.3 Sample Result Reports

5.4 Data Qualifying Flags

Sample report results are qualified with data qualifying flags. These flags have the following definitions:

U: The analyte of interest was not detected, to the limit of detection indicated.

B: The analyte of interest was detected in the method blank associated with the sample, as well as in the sample itself. The B flag is applied without regard to the relative concentrations detected in the blank and sample.

J: The analyte of interest was detected below the practical quantitation limit. This value should be regarded as an estimate.

D: The value reported is derived from the analysis of a diluted sample or sample extract.

P: When a dual column GC technique is employed, this flag indicates that calculated results from the two columns differ by more than 25%. Generally, we report the lower value.

E: The value reported is based on a sample or sample extract in which the target analyte concentration exceeded the calibration range. The value reported should be considered an estimate.

C: The target analyte's presence was confirmed by GC/MS.

6. Quality Control

Refer to Appendix V for detailed QA and corrective action requirements.

6.1 Initial Calibration

6.1.1 Criteria

Initial calibration data can be evaluated in one of two ways: %RSD of the calibration factors (CF) or correlation coefficient of a linear regression analysis. CFs are calculated using the equation:

$$CF = \frac{\text{response}}{\text{ng injected}}$$

The distinctions between these methods are: the %RSD method assumes a linear response with the calibration curve passing through the origin; the linear regression method assumes a linear response with an unforced intercept.

Laucks employs the use of calibration factors. The %RSD must be less than 20% for all compounds.

6.1.2 Corrective action

If the criteria are not met, the instrument must be recalibrated.

6.1.3 Documentation

Copies of the calibration standards and the calculated %RSDs are stored with the raw data. If the initial calibration can not be used, this information is noted in the instrument logbook.

6.2 Initial Calibration Verification

6.2.1 Criteria

The ICV is used to establish the retention times for all target analytes. The CF for each compound is calculated and the percent difference is calculated as detailed below. The %D results cannot exceed 15%.

6.2.2 Corrective action

If the %D criteria are not met, no samples can be analyzed. Perform system maintenance and re-check the ICV. If the criteria still cannot be met, the system must be recalibrated.

6.2.3 Documentation

Copies of the calibration standards and the calculated %Ds are stored with the raw data. If the calibration standard is cannot be used, this is documented in the instrument logbook.

6.3 Continuing Calibration Verification

6.3.1 Criteria

After every ten injections, a CCV standard is analyzed. The CF for each compound is calculated and the percent difference is calculated as follows:

$$\%Difference = \frac{CFv - \overline{CF}}{\overline{CF}} \times 100$$

where:

CF_v= CF from the analysis of the verification standard.

$\overline{CF}$ = Average CF from the initial calibration.

The %D results cannot exceed the detailed CCV criteria of 15%.

The retention times for all target analytes must fall within the RT windows.

6.3.2 Corrective action

Check calculations, examine the chromatogram, check the integration, re-analyze another CCV, or perform instrument maintenance. To validate the quantitation of target analytes in analytical samples, the samples must be bracketed by in-control CCVs. However, CCV CFs can be outside the control limits as long as the corresponding samples contain no detectable levels of the target analyte for which the CF is out of control and the CF value exceeds the upper control limit (i.e., there is increased sensitivity). Algebraically, this means a greater negative percent difference than the control limit.

6.3.3 Documentation

Copies of the continuing calibration standards and the calculated %Ds are stored with the raw data. If the continuing calibration standard cannot be used, this information is noted in the instrument logbook.

6.4 Method Blank

6.4.1 Criteria

A method blank is used to verify contamination free reagents and apparatus. A method blank is analyzed following every CCV and prior to sample analysis. Method blank control limits are reporting limit for analytes with the exception of the common laboratory solvent methylene chloride. The control limit for this analyte is 2 x reporting limit.

Where contractually required, such as Navy samples, analytes present must be the MDL.

6.4.2 Corrective action

Corrective action in the form of reanalysis of the method blank prior to sample analysis is performed when target analytes are present above the reporting limit. Out-of-control surrogate recoveries in the method blank require reanalysis of the method blank. In any event it is the laboratory's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the chromatograms be minimized. In the extreme case of chronic contamination, method blanks may have to be analyzed from each stage of the sample processing to determine the contamination source so it can be eliminated.

6.4.3 Documentation

Copies of all method blank analyses are stored with the sample analyses raw data. In addition, the raw data for the method blank analyses are stored in the laboratory for an extended period of time. The results for the method blank analyses are reported electronically via the laboratory's LIMS database. If a method blank cannot be used, this information is noted in the instrument logbook.

6.5 Blank Spike or QC Check Sample (LCS)

6.5.1 Criteria

A blank spike follows the same protocol as a matrix spike analysis except that the spiking solution is added to an aliquot of PFW instead of an actual sample. A method blank with added analytes is a blank spike. A blank spike is the same as a QC check standard.

6.5.2 Corrective action

The blank spike is used to determine whether a method is in control during sample preparation and analysis. Sample reanalysis would be triggered by an out of control blank spike only if the sample surrogate recoveries and MS/MSD spike recoveries indicated sample processing errors.

6.5.3 Documentation

The raw data for the blank spike analyses are stored in the laboratory for an extended period of time. The results for the blank spike analyses are reported electronically via the laboratory's LIMS database. If data from the blank spike analysis cannot be used, this information is noted in the instrument logbook.

6.6 Matrix Spike

6.6.1 Criteria

A sample is chosen at random from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to analysis. A matrix spike analysis is performed with each analytical batch, up to a maximum of 20 samples. The matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$\%Recovery = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Concentration in spiked sample.
SR = Native concentration in unspiked sample.
SA = Concentration of spike added.

6.6.2 Corrective action

Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action may involve recalculation and/or reanalysis. This process should also include evaluation of the recovery of surrogate compounds in the MS sample and recovery of matrix spiking compounds from the blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

6.6.3 Documentation

The raw data for the matrix spike analyses are stored with the sample analyses raw data. The results for the matrix spike analyses are reported electronically via the laboratory's LIMS database.

6.7 Matrix Spike Duplicate

6.7.1 Criteria

A matrix spike duplicate analysis is performed with each analytical batch, up to a maximum of 20 samples. The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used to measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values. This calculation is as follows:

$$RPD = \frac{S1 - S2}{(S1 + S2)/2} \times 100$$

where:

S1 = Measured concentration for MS sample.
S2 = Measured concentration for MSD sample.

6.7.2 Corrective action

If a trend in out-of-control RPD values is observed, the method used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility.

6.7.3 Documentation

The raw data for the matrix spike duplicate analyses are stored with the sample analyses raw data. The results for the matrix spike duplicate analyses are reported electronically via the laboratory's LIMS database.

6.8 Surrogate Recovery

6.8.1 Criteria

Surrogates are chemically similar compounds added to every sample, method blank, and QC sample prior to sample processing. They are used to monitor potential sample processing errors and matrix effects. Surrogate compound recoveries are calculated as follow:

$$\% \, Recovery = \frac{S_m}{S_a} \times 100$$

where:

S_m = Concentration of surrogate measured in sample.
S_a = Concentration of surrogate added.

6.8.2 Corrective Action

Check calculations for possible error. Reanalysis is required for surrogate recoveries which exceed the established control limits, unless matrix interference is observed or surrogates are diluted out.

Out-of-control surrogate recoveries in the method blank require that the method blank be reanalyzed. Sample analyses are not performed until all criteria are met in the method blank analysis. Sample and QC analyses require reanalysis for out-of-control surrogate recoveries. If the sample analyses demonstrate out-of-control surrogate recoveries due to matrix interference, this corrective action is discussed in the narrative.

6.8.3 Documentation

The surrogate recoveries for all samples, blanks, and QC analyses are reported electronically via the laboratory's LIMS database.

7. References

SW 846 - Test Methods for Evaluating Solid Waste - Method 8000B "Determinative Chromatographic Separations", USEPA - Office of Solid Waste and Emergency, Revision 2, December 1996.

SW 846 - Test Methods for Evaluating Solid Waste - "Non-Halogenated Organics using GC/FID", Method 8015B, USEPA - Office of Solid Waste and Emergency Response, Revision 2, December 1996.

SW 846 - Test Methods for Evaluating Solid Waste - "Purge and Trap", Method 5030B, U.S. EPA, Revision 2, December, 1996.

SW 846 - Test Methods for Evaluating Solid Waste - "Purge and Trap", Method 5035, U.S. EPA, December, 1996.

SW 846 - Test Methods for Evaluating Solid Waste - "Organic Analytes", Chapter Four, U.S. EPA, December, 1996.

APPENDIX I

Target Analytes And Surrogates

Analytes
Isobutyl alcohol
Propionitrile
Acetonitrile
1,4-Dioxane*
Surrogates
Trifluorotoluene*
Bromofluorobenzene

* These two compounds co-elute. Therefore, when 1,4-dioxane is requested as a target analyte, the surrogate, trifluorotoluene is omitted from the analysis.

Appendix II

Initial Calibration Concentrations (µg/L)*

Compound	STD1	STD2	STD3	STD4	STD5
Isobutyl alcohol	300	200	100	80	40
Acetonitrile	300	200	100	80	40
Propionitrile	300	200	100	80	40
Trifluorotoluene	40	30	20	10	4
1,4-Dioxane	3000	2000	1000	500	100
Bromofluorobenzene	40	30	20	10	4

* At the time of this writing, these are the current calibration standards, however, they are subject to change.

APPENDIX III

Analysis Sequence

Injection	Sample
1	IBLK
2	Std 1
3	Std 2
4	Std 3
5	Std 4
6	Std 5
	Method Blank
	A total of 10 samples and/or blanks, duplicates or matrix spike samples.
	CCV
	IBLK
	A total of 10 samples and/or blanks, duplicates or matrix spike samples.
	A closing CCV

APPENDIX IV

Data Packet Check List

I. CLIENT DELIVERABLE - IF REQUESTED

II. QC SUMMARY

_____ Surrogate Recovery Summary Report
_____ Method Blank Report
_____ Blank Spike Report
_____ MS/MSD Report
_____ Method Blank Summary Report

III. SAMPLE DATA:

(In numerical order)

_____ Sample Data Report	
_____ Sample Confirmation Form	
_____ Chromatograms	Primary
_____ Quantitation Report	Primary
_____ Chromatograms	Secondary
_____ Quantitation Report	Secondary

IV. STANDARD DATA:

(In chronological order)

_____ Linearity Report	Primary/Secondary
_____ CCV Reports, %Difference	Primary/Secondary

Linearity Standards:

_____ Chromatograms	Primary
_____ Quantitation Report	Primary
_____ Chromatograms	Secondary
_____ Quantitation Report	Secondary

Continuing Calibration Standards:

_____ Chromatograms	Primary
_____ Quantitation Report	Primary
_____ Chromatograms	Secondary
_____ Quantitation Report	Secondary

Multiple Component Standards (if required):

_____ Chromatograms	Primary
_____ Quantitation Report	Primary
_____ Chromatograms	Secondary
_____ Quantitation Report	Secondary

Other Standards Used to Support Sample Data (if required):

_____ i.e., MDL Reports

V. Raw QC Data:

_____ Method Blank Report
_____ Confirmation Form
_____ Chromatograms Primary
_____ Quantitation Report Primary
_____ Chromatograms Secondary
_____ Quantitation Report Secondary

_____ Blank Spike Report
_____ Confirmation Form
_____ Chromatograms Primary
_____ Quantitation Report Primary
_____ Chromatograms Secondary
_____ Quantitation Report Secondary

_____ Matrix Spike Report
_____ Confirmation Form
_____ Chromatograms Primary
_____ Quantitation Report Primary
_____ Chromatograms Secondary
_____ Quantitation Report Secondary

_____ Matrix Spike Duplicate Report
_____ Confirmation Form
_____ Chromatograms Primary
_____ Quantitation Report Primary
_____ Chromatograms Secondary
_____ Quantitation Report Secondary

_____ Control Charts (optional)

VI. Bench Sheets

_____ Injection Log
_____ Sequence
_____ Extraction Bench Sheets
_____ Misc. Work Sheets. i.e., %TS, SDG summary, calcs, HTVR,
_____ Standards Log for all standards used with work

VII. Reject Data:

DO NOT COPY DO NOT PAGINATE

Acquired data not used to support sample results.

APPENDIX V

Analyte Elution Order

Column: DB-624	Column: DB-VRX
Acetonitrile	Acetonitrile
Propionitrile	Propionitrile
Isobutyl alcohol	Isobutyl alcohol
Trifluorotoluene*	Trifluorotoluene*
1,4-Dioxane*	1,4-Dioxane*
Bromofluorobenzene	Bromofluorobenzene

* These two compounds co-elute. Therefore, when 1,4-dioxane is requested as a target analyte, the surrogate, trifluorotoluene is omitted from the analysis.

APPENDIX VI

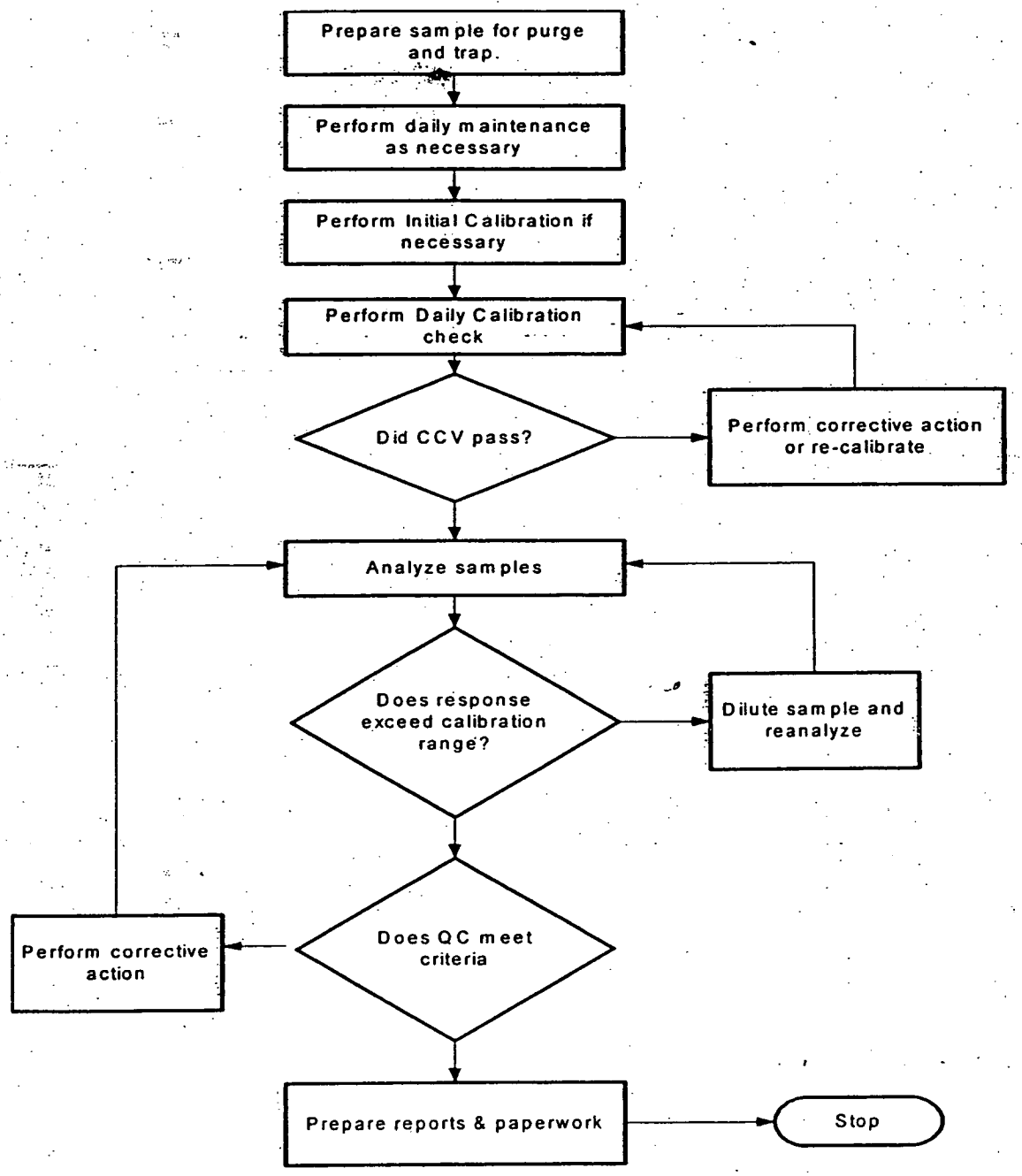
Method 8015B QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Holding Time	14 days from collection.	14 days from collection.	N/A	N/A	HTVR (holding time violation report) filed with data and noted in file and narrative.
Initial Calibration Curve	Minimum of 5 levels. If %RSD < 20, linearity assumed and average RF used. Alternatively use linear regression to determine linearity.	Minimum of 5 levels. If %RSD < 20, linearity assumed and average RF used.	Initially, and until ICV fails.	Reanalysis of out of control standards.	Copies of all raw data are filed.
Initial Calibration Verification	Mid-level calibration standard run every 10 samples. If not within ± 15%, recalibrate.	Mid-level calibration standard run every 10 samples. If >15%D, reanalyze or recalibrate. RT are updated from this standard for all subsequent analyses.	At the beginning of every QC period.	Reanalysis of ICV in order to meet %D criterion. If reanalysis does not meet criterion, analyze initial calibration curve.	Copies of raw data filed and noted in instrument logbook.
Continuing Calibration Verification	Mid-level calibration standard run every 10 samples. If not within ± 15%, recalibrate. Standard RT must fall within daily window or system is out of control.	Mid-level calibration standard run every 10 samples. If > 15%D, reanalyze for any analyte out of control analyte which is detected in associated sample analysis. Standard RT must fall within daily window or system is out of control.	Every 10 samples.	Samples injected after criteria was exceeded must be reanalyzed.	Copies of raw data filed and notated in instrument logbook.
Internal Standards	Optional.	No internal standards are used at this time.			
Method Blank	One method blank per batch of up to 20 samples, or when there is a change in reagents; whichever is more frequent. Analysis of the method blank should demonstrate that interferences from the analytical system, glassware and reagents are under control.. Analytes present should be < MDL.	< RL for all analytes. Where contractually required, analytes present must be < MDL.	One method blank per batch of up to 20 samples.	Samples may not be analyzed until all criteria for the method blank are met.	Copies of raw data filed, and reported electronically. Daily control charts for all method blanks are recorded.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Surrogate Standards	Add surrogates to encompass range of temperature program. Results must fall within laboratory established control limits.	4-Bromofluorobenzene and/or trifluorotoluene. Percent recoveries must meet established laboratory control limits. See control limits catalog for laboratory established control limits.	Surrogates are used in all standards, blanks, samples, and QC.	Reanalysis if surrogate recoveries exceed the established control limits. If reanalysis produces similar surrogate recoveries, then it may be due to matrix interference.	Any out of control surrogates are documented in associated file.
MS/MSD & Blank Spike	One MS/MSD per 20 samples or each batch of samples, whichever is more frequent. Compare results to Table in method.	Blank spike recoveries, MS/MSD recoveries and RPDs must meet control limits established by laboratory. See control limits catalog for laboratory established limits.	One blank spike and one set of MS/MSD daily.	Reanalysis of blank spike and MS/MSD unless matrix effect has already been demonstrated.	MS/MSD recoveries are stored electronically. Raw data is stored with file. Out of control events are notated in file.
Sample Preservation and Storage	Water samples: pH ≤ 2 with HCL. All samples: store at 4° C.	Water samples: pH ≤ 2 with HCL. All samples: store at 4° C.	All water samples are to be preserved. Any samples to be stored at 4°C.	The pH is measured for all water samples. Client is notified if aqueous samples are not acid-preserved. pH cannot be determined until after analysis in order to maintain sample integrity.	pH of all water samples recorded in instrument logbook.
Standard Solution Expiration	Stock standards: 6 months. Store at 4° C with minimum headspace, away from light. Aqueous calibration standards: 1 hour, 24 hours if stored with zero headspace.	Stock standards: 6 months; Stored -10° to -20° C. Aqueous calibration standard: daily.			All standard data recorded in standard logbook.
Field Sample Amount Required	Water samples: 2 40 mL vials with zero headspace. Soils: glass, with Teflon-lines lids.	Water samples: 2 40 mL vial with zero headspace. Soil samples: 2 oz. glass containers, Teflon-lined lids.			Bottles received by laboratory documented electronically.
Applicability	Groundwaters, soils, sludges, water-miscible and non-water miscible wastes.				

APPENDIX VII

Flow Chart



LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8084

Title: **Analysis of Organochlorine Pesticides and PCBs by SW846 Methods 8081B and 8082A**

Revision history:

Number	Date
0	2/11/98
1	7/10/98
2	4/29/99
3	4/27/00

Controlled Document

No. 20 **Assigned to:** Tetra

Revised by: Monica Carr, Organic Division Manager — Date: 4/28/00

Approved by: Kathy Kreps, Laboratory Director — Date: 04/28/2000

Approved by: Harry Romberg, QA Officer — Date: 04-28-2000

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1. Introduction and Scope

1.1 Method Description

1.1.1 This SOP describes the procedures and specifications for instrumental analysis of various organochlorine pesticides and polychlorinated biphenyls (PCBs) in water and soil following SW846 Methods 8081B and 8082A. Analysis is performed by gas chromatography using a single injection port and splitting into dual GC columns with electron-capture detectors. This system provides quantitation and confirmation of pesticides and Aroclors (PCBs) from a single injection. The following table lists the compounds that may be determined by these methods. Additional compounds, listed in Method 8081B, may also be determined.

SW8081B ROUTINE COMPOUNDS	
alpha-BHC	beta-BHC
delta-BHC	gamma-BHC (Lindane)
Heptachlor	Aldrin
Heptachlor epoxide	Endosulfan I
Dieldrin	4,4'-DDE
Endrin	Endosulfan II
4,4'-DDD	Endosulfan sulfate
4,4'-DDT	Methoxychlor
Endrin aldehyde	Endrin ketone
alpha-Chlordane	gamma-chlordane
Toxaphene	
SW8081B OPTIONAL COMPOUNDS	
**Chlordane (not otherwise specified)	Isodrin
Simazine	Atrazine

**When chlordane is requested, a technical chlordane multicomponent standard is analyzed and response factors are calculated for 3-5 major peaks (including the alpha- and gamma-isomers). If these peaks are present in the sample at similar ratios to those found in the technical chlordane standard, an average concentration is calculated from the peaks chosen for calibration. If the peaks are present in the sample at dissimilar ratios to those found in the technical chlordane standard, a calibration factor will be calculated for the standard based upon the sum of the responses for each of the peaks and the sample concentration will be calculated based on the sum of the same peaks in the sample.

SW8082A COMPOUNDS	
Aroclor-1016	Aroclor-1221
Aroclor-1232	Aroclor-1242
Aroclor-1248	Aroclor-1254

Aroclor-1260	

1.1.2 Method Deviations: The analyte list is based on a combination of Method 8081B and 8082A analytes. Additional analytes are only added if requested by the client(s).

1.1.3 This method is restricted to use by, or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of chromatograms. Each analyst performing this method must have demonstrated the ability to perform the described chromatographic analysis and/or data interpretation.

1.1.4 In some instances, samples being analyzed for PCBs will require sulfuric acid cleanup. In instances where samples are being analyzed for both pesticides and PCBs, an aliquot is separated prior to the sulfuric acid cleanup step, and is analyzed for pesticides only. The separation of aliquots prior to this cleanup will prevent the potential loss of target pesticide compounds.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1 Samples are normally collected in glass containers with Teflon-lined caps. All samples and sample extracts are stored at 4°C±2°C. Water samples must be extracted within 7 days of sample collection, soil samples within 14 days of sample collection. All extracts must be analyzed with 40 days of sample preparation.

1.3 Definition of Terms

1.3.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

Batch Identifier	A number given to each preparation or analysis group which uniquely identifies that batch. This number is generally the blank ID for preparation batches and either a sequence number for organic analyses or an analysis number which is similar to the blank ID, only preceded by an "A" rather than a "B" for inorganic batches. The preparation batch IDs are discussed in other documentation.

Blank spike	A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts of target analytes and surrogates are added each time sample extracts are prepared. Blank spikes are required on all HAZWRAP and NFESC work. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard.
CCV	Continuing calibration verification. This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency during the analysis sequence to verify that the instrument has remained in calibration.
CF	Calibration factor. The ratio of analyte instrument response to nanograms injected. This term is defined in the same way in both the CLP contract and SW 846.
CLP	Contract Laboratory Program. The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In the context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.
DIW	Deionized water. Lab reagent water. Organic-free water. Since the systems used to provide DIW at Laucks all contain carbon polishing filters, they are capable of providing organic-free water for use in method blanks and blank spikes.
IBLK	Instrument blank. This term is borrowed from CLP. Blank solvent containing the method surrogates is injected into the instrument to monitor for carry over between sample extract injections.
ICV	Initial calibration verification. It is a standard which is injected at the start of each QC period that is compared to the initial multi-point calibration to determine whether the instrument is still in calibration.
IDL	Instrument detection limit. The lowest concentration of a target analyte that will yield a signal:noise ratio of at least 3x. Used as a starting point for selecting MDL study spiking levels.

MDL	Method detection limit. The lowest concentration in a sample which will yield a positive result that is greater than zero at a known level of confidence. MDLs are empirically determined by Laucks.
MDL standard	Method detection limit standard. A standard prepared so that the concentrations of the target analytes are in the range of 1x to 4x the empirically determined MDLs on an extract/digest basis. This standard is used to verify that the instrument is capable of detecting the target analytes on an ongoing basis.
PQL or Reporting Limit	Practical Quantitation Limit or Reporting Limit- The value used when reporting a non-detect. It may be administratively, empirically or contractually set.
QC check standard	Quality control check standard. Referred to in this SOP as a blank spike. A QC check standard is a requirement of SW 846 method 8000 and is used to determine whether the analytical system is in control if MS/MSD recoveries are out of control. See also blank spike.
QC period	Quality control period. An analysis sequence initiated by the analysis of one or more standards, followed by sample extracts/digests, and terminated with a standard analysis. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP.
Reporting Limit (RL)	The reporting limit is defined by the low level standard, also referred to as the practical quantiation limit (PQL).
RSD or %RSD	Relative standard deviation or percent relative standard deviation. The ratio of the standard deviation of a set of values to the mean of the set of values expressed as a percentage. A measure of the similarity of the values one to another.
RT, Retention time	The time (in minutes) at which a target analyte elutes from a chromatography column.

RT window	Retention time window. The +/- value which is applied to the ICV to establish the time range used to make tentative compound identifications.
Sequence	A set of sample extracts/digests and standard solutions introduced into an instrument in a chronologically continuous group. See also QC period.
SRM	Standard Reference Material - A material containing known quantities of target analytes in a homogeneous matrix which approximates the matrix of the samples being analyzed. It is used to establish that the analytical process is in control.

2. Equipment List and Standards

2.1 Chromatographic System

2.1.1 This analysis requires a gas chromatograph with a programmable oven, heated injection port, dual electron-capture detectors, autosampler and an electronic data-acquisition system.
Equipment list:
Gas chromatograph (Hewlett-Packard 5890 / 5890A)
Autosampler (Hewlett-Packard 7673A)
2 electron-capture detectors (Hewlett-Packard)
2 capillary chromatographic columns of dissimilar phase (J&W DB5 and DB608, 30m x 0.53mm megabore, or equivalents).
Helium carrier gas
5% methane/95% argon detector make-up gas

2.2 Standards

2.2.1 Commercially prepared, certified stock standards are used to prepare working solutions for all surrogates, calibration mixes, and spike mixes. The 2 calibration mixes (INDA and INDB) contain all of the individual pesticide analytes. The spike mix contains 6 representative individual pesticides. These are ordered from Restek, Supelco or an equivalent supplier. Stock standards must be replaced by the manufacturers expiration date.

2.2.2 Calibration standards are prepared at 5 different concentration levels by dilution of the stock standards with hexane. High level INDA and INDB mixtures are made at 16 times the PQL concentration. The lower levels are diluted by factors of 2, 4, 8 and 16. They must be replaced after 6 months or by the expiration date of the material they were made from, whichever is earlier.

2.2.3 Multicomponent analyte calibration standards (Aroclors, chlordane, Toxaphene), with the exception of Aroclors 1016 and 1260, are prepared at one concentration level, by dilution of commercially-purchased stock solutions in hexane. Standards of the Aroclors 1016 and 1260 are combined in a mixture and prepared at five concentration levels. These must be replaced after 6 months or by the expiration date of the material they were made from, whichever is earlier.

2.2.4 A breakdown evaluation (EVAL) mix is prepared from dilution of stocks of 4,4'-DDT and endrin with hexane.

2.2.5 A surrogate mix is prepared from neat materials and contains 2,4,5,6-tetrachloro-meta-xylene (TCMX) and decachlorobiphenyl (DCB). These standards are made in hexane and added to all standard mixes (before dilution if applicable).

2.2.6 Refer to SOP LTL-1013 (Preparation, Storage, Shelf Life and Traceability Documentation of Standards and Reference Materials) for detailed instructions on standards preparation and storage.

2.2.7 Appendix I details the compounds and concentrations contained in all solutions.

3. Safety precautions and Waste Disposal

3.1 Routine Safety Precautions

3.1.1 All standards and sample extracts should be handled as if they contain hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.4 Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.5 The electron-capture detectors used in this analysis contain a radioactive source and should not be opened or otherwise tampered with.

3.2 Waste disposal

3.2.1 Solvent wastes generated in using this procedure (expired standards, old sample extracts, rinsates, etc.) should be emptied into the solvent waste container in the fume hood.

3.2.2 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

4. Calibration and Quality Control

4.1 QA Requirements and Corrective Action

4.1.1 Detailed in the following sections are applicable QA requirements and subsequent corrective actions to be applied to this analysis. A summary of these requirements can be found in Appendix IV.

4.2 Method Detection Limit Study

4.2.1 Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in the Laucks SOP on MDLs, located in the SOP manual. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration near the anticipated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL.

4.3 Method Validation

4.3.1 Prior to the analysis of any samples, it is necessary to validate the method. A method validation study is performed in a similar manner to an MDL study with the exception that a minimum of 4 replicates are required and the concentration levels are typically higher.

4.3.2 The precision of spike recoveries must meet or exceed the criteria tabulated in SW 846.

4.4 Retention Time Windows

4.4.1 Retention time window studies are conducted following the Laucks SOP on Establishing RTWs and the procedure detailed in SW 846, Method 8000B, which defines a window for each single and multi- component analyte based on the retention times taken from three standard injections over a 72 hour period.

4.4.2 The retention time window half-width is set at 3 times the above calculated standard deviation. This operation must be repeated whenever major equipment changes are made, whenever the chromatographic method is significantly modified, or whenever a column is replaced.

4.4.3 The calculated retention time window half widths are typically unrealistic values. Therefore RT windows have been administratively set at the values listed in OLM03.1 for megabore analyses (see table below) and at ±0.03 for capillary analyses. These values are typically wider than 3 times the standard deviation as determined above, but are more realistic.

Analyte	Megabore	Capillary
alpha-BHC	±0.05	±0.03
beta-BHC	±0.05	±0.03
gamma-BHC (Lindane)	±0.05	±0.03
delta-BHC	±0.05	±0.03
Heptachlor	±0.05	±0.03
Aldrin	±0.05	±0.03
alpha-Chlordane	±0.07	±0.03
gamma-Chlordane	±0.07	±0.03
Heptachlor epoxide	±0.07	±0.03
Dieldrin	±0.07	±0.03
Endrin	±0.07	±0.03
Endrin aldehyde	±0.07	±0.03
Endrin ketone	±0.07	±0.03
4,4'-DDD	±0.07	±0.03
4,4'-DDE	±0.07	±0.03
4,4'-DDT	±0.07	±0.03
Endosulfan I	±0.07	±0.03
Endosulfan II	±0.07	±0.03
Endosulfan sulfate	±0.07	±0.03
Methoxychlor	±0.07	±0.03
Tetrachloro-m-xylene	±0.07	±0.03
Decachlorobiphenyl	±0.10	±0.03
Isodrin	±0.07	±0.03
Aroclors	±0.07	±0.03
Toxaphene	±0.07	±0.03
Chlordane	±0.07	±0.03

4.5 Breakdown Evaluation (only required when analyzing for pesticides)

4.5.1 At the beginning of each analysis sequence an evaluation (EVAL) mix must also be analyzed. This is a mid-level standard containing 4,4'-DDT and endrin, and is examined for the breakdown products of these analytes (4,4'-DDD, 4,4'-DDE, endrin aldehyde, endrin ketone) which indicate the need for GC system maintenance. The percent breakdown must be less than 15% for both Endrin and 4,4'-DDT.

4.6 Initial Multi-Point Calibration for Pesticides and PCBs

4.6.1 Analyze single component pesticide standards using at least 5 different concentration levels for linear calibrations. The lowest concentration should be at a concentration near, but

above, the method reporting limit or PQL. The highest concentration should define the upper usable working range of the detector.

4.6.2 Analyze multi-component pesticide and PCB standard solutions at one concentration level, with the exception of the Aroclor 1016/1260 mixed standard. This standard should be analyzed at 5 different concentration levels for linear calibration. This step can be omitted if analyzing for pesticides only.

4.6.3 SW 846 allows the use of both linear and non-linear models for the calibration data. The option for non-linear calibration may be necessary to achieve low detection limits or to address specific instrumental techniques.

4.6.4 The choice of a specific calibration model should be made in one of two ways. The first is to begin with the simplest approach, the linear model through the origin, and progressing through the other options until the calibration acceptance criteria are met. The second approach is to use *a priori* knowledge of the detector response to choose the calibration model. Such knowledge may come from previous experience, knowledge of physics of the detector, or specific manufacturer's recommendations.

4.7 Linear Calibration

4.7.1 External standard initial calibration data is evaluated by determining the %RSD of the calibration factors.

4.7.2 CFs are calculated using the equation:

$$CF = \frac{\text{response}}{\text{ng injected}}$$

4.7.3 The calculated CFs are tabulated and the %RSD calculated. There are no compound-specific criteria. All %RSDs must be within 20% for each analyte or averaged across all analytes in the calibration standard mix. Laucks uses 40% percent as the upper limit for all compounds as an internal guideline although it is not a requirement of SW 846.

4.7.4 Corrective action

4.7.4.1 If the criteria are not met, the instrument must be re-calibrated.

4.8 Non-linear Calibration

4.8.1.1 In situations where the analyst knows that the instrument response does not follow a linear model over a sufficiently wide working range, or when the other approcahes described here have not met the acceptance criteria, a non-linear calibration model may be employed.

4.8.1.2 When using a calibration model for quantitation, the curve must be continuous, continuously differentiable and monotonic over the calibration range. The model chosen should have no more than four parameters, i.e., if the model is polynomial, it may be no more than third order, as in the equation:

$$y = ax^3 + bx^2 + cx + d$$

4.8.1.3 The statistical considerations in developing a non-linear calibration model require more data than the more traditional linear approaches. A quadratic (second order) requires a minimum of six standards, and a third order polynomial requires seven standards. Do not force the line through the origin, i.e., do not set the intercept as 0, and do not include the origin (0,0) as a calibration point.

4.8.1.4 Whichever option is employed, a surrogate concentration must fall within the calibration range.

4.8.2 A set of three to five major peaks is selected for each multicomponent analyte. These should be characteristic of the multicomponent analyte in question. Retention time windows and calibration factors are generated for each of the peaks chosen.

4.8.3 Corrective action

4.8.3.1 If the criteria are not met, the instrument must be re-calibrated.

4.9 Initial Calibration Verification

4.9.1 Concentration and/or CF Criteria

4.9.1.1 At the beginning of an analysis sequence analyze a mid-range calibration standard. The computed calibration factor (CF) or concentration measurement must meet the criteria detailed below.

4.9.1.2 Using the appropriate calculation technique (average CF) compute either CFs or concentration values. For linear calibrations the ICV standard can be verified by calculating either the percent difference or the percent drift.

4.9.1.2.1 The percent difference calculation compares the ICV CFs to the mean CFs from the initial multi-point calibration. The percent difference is calculated as follows:

$$\%D = \frac{Cv - \overline{CF}}{\overline{CF}} \times 100$$

where:

C_v = Calibration Factor

CF = Mean Calibration Factor

4.9.1.2.2 The percent drift calculation compares the ICV calculated concentrations to the theoretical (or actual) concentration of the ICV standard. The percent drift is calculated as follows:

$$\%D = \frac{C_c - C_T}{C_T} \times 100$$

where:

C_c= Calculated Concentration
C_T = Theoretical Concentration

4.9.1.3 There are no compound-specific criteria. The %D results should be within ±15% of the average CF or expected concentration from the initial calibration for each analyte, or averaged across all analytes in the continuing calibration standard.

4.9.2 Corrective action

4.9.2.1 If the ICV criteria are not met, no sample extracts can be analyzed. Perform system maintenance and re-check the ICV. If the criteria still cannot be met, the system must be recalibrated.

4.10 Updating Retention Time Windows

4.10.1 The retention time windows for compound identification are updated using the retention times for each target analyte in the ICV standard as the center of the window and the previously determined retention time window half-width to establish the retention time range to be used for compound identification.

4.11 Instrument Blank

4.11.1 Criteria

4.11.1.1 Any sample that is suspected of containing high concentrations of target analytes should be followed by an IBLK or solvent rinse. This IBLK analysis is used only to make a judgment as to the possibility of carry-over into the sample extract immediately following the IBLK. Evaluation criteria are detailed below.

4.11.2 Corrective action

4.11.2.1 IBLKs used to monitor for possible carryover in high concentration extracts (those IBLKs optionally placed into the sequence following suspected high concentration extracts) are used to flag the possibility of analyte carryover into the following sample extract. The extract immediately following the out of control IBLK may need to be re-analyzed if there is a detectable amount of the analyte found in the IBLK.

4.12 Continuing Calibration Verification

4.12.1 A mid-range calibration standard is analyzed at the frequency of every 10 samples, or every 12 hours, whichever is sooner. In addition, this standard must be the last injection made in the analysis sequence.

4.12.2 Criteria

4.12.2.1 After every 10 sample extract injections, a CCV standard is analyzed. The CF or concentration for each analyte is calculated and the percent difference or percent drift is calculated as shown above.

4.12.2.2 The %D results should be within ±15% of the average CF or expected concentration from the initial calibration for each analyte, or averaged across all analytes in the continuing calibration standard.

4.12.2.3 The retention times for all target analytes must fall within the RT windows established by the ICV.

4.12.3 Corrective action

4.12.3.1 Check calculations or perform instrument maintenance. To validate the quantitation of target analytes in analytical samples, the samples must be bracketed by in-control CCVs. However, CCV CFs can be outside the control limits as long as this was due to an increase in response and the corresponding samples contain no detectable levels of the target analyte for which the CF is out of control.

4.13 Method Blanks

4.13.1 Criteria

4.13.1.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples extracted at the same time or one blank every 20 samples which ever is more frequent. Any analyte response above the reporting limit is reported.

4.13.2 Corrective action

4.13.2.1 Corrective action may necessitate re-extraction of the sample set. For example, if an analyte were found in the blank but not in any of the associated samples then the sample group may not require re-extraction. In any event it is the laboratory's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the chromatograms be minimized. In the extreme case of chronic contamination, blanks may have to be analyzed from each stage of the sample processing to determine the contamination source so it can be eliminated. In all cases where blank contamination

exceeds the control limit a narrative comment must be made which documents the corrective actions taken.

4.14 Blank Spikes

4.14.1 Criteria

4.14.1.1 A blank spike follows the same protocol as with the matrix spike analysis except that the spiking solution is added to a method blank solution instead of an actual sample. A method blank with added analytes is a blank spike. A blank spike is the same as a QC check standard. It is recommended that all single component pesticide target analytes of concern and a minimum of one Aroclor be spiked into the LCS. A subset of the single-component target analytes can be substituted for the full list if specified in project-specific contracts or workplans per the USACOE Shell document. In addition, the LCS and matrix spike should consist of the same components at the same concentration levels in order to accurately evaluate matrix interference in the MS/MSD samples.

4.14.1.2 Blank spike recoveries must meet the criteria specified in the quality control database, QC_DB.

4.14.2 Corrective action

4.14.2.1 The blank spike is used to determine whether a method is in control during sample preparation and analysis. Sample re- extraction and re-analysis would be triggered by an out of control blank spike only if the sample surrogate recoveries and MS/MSD spike recoveries indicated sample processing errors.

4.15 Matrix Spike

4.15.1 Criteria

4.15.1.1 A sample is chosen at random from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to extraction. It is required that a matrix spike analysis be performed with each extraction batch. The minimum frequency for MS analysis is 1 each per 20 samples per matrix. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$\%\text{Recovery} = \frac{MS - SA}{S} x100$$

where:

MS = concentration in spiked sample
SA = native concentration in unspiked sample
S = spike amount

4.15.1.2 The recovery criteria are detailed in the QC database, QC_DB. In the instance that the native target analyte concentration is greater than 5x the spike concentration, the MS recovery control limits do not apply. In this case, treat the MS/MSD pair as duplicates and report them as such in the quality control database.

4.15.2 Corrective action

4.15.2.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action may involve recalculation, re-extraction, and/or reanalysis. This process should also look at the recovery of surrogate compounds in the MS sample and at the recovery of matrix spiking compounds from the extraction batch blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.16 Matrix Spike Duplicate

4.16.1 Criteria

4.16.1.1 The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used to measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values. This calculation is as follows:

$$\%RPD = \frac{|\chi - \delta|}{(\chi + \delta)/2} x100$$

where:

χ = measured concentration for MS sample
δ = measured concentration for MSD sample

4.16.1.2 RPD control limits are detailed in the QC database, QC_DB.

4.16.2 Corrective action

4.16.2.1 If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility.

4.17 Surrogate Recovery

4.17.1 Criteria

4.17.1.1 Surrogates are chemically similar compounds added to every sample, method blank, and QC sample prior to sample processing. They are used to monitor for potential sample processing errors and matrix effects. Surrogate compound recoveries are calculated as follows:

$$\% \text{ recovery} = \frac{S_m \times 100}{S_a}$$

where:

S_m = concentration of surrogate measured in extract
S_a = concentration of surrogate added

4.17.1.2 Detailed surrogate recovery control limits are tabulated in the QC database, QC_DB.

4.17.2 Corrective Action

4.17.2.1 Check calculations for possible error. Low surrogate recoveries are greater potential indicators of poor method performance than high surrogate recovery since non-GC/MS methods cannot separate co-eluting interferences. Hence corrective action is not required for high surrogate recoveries.

4.17.2.2 Low surrogate recoveries in the method blank may require that all the samples in the associated batch be re-extracted and re-analyzed. In any case, it is imperative to identify the problem associated with low recovery so that it can be corrected. It is a requirement that all out of control surrogate recoveries and the corrective action taken be discussed in the narrative.

5. Operation procedures

5.1 Chromatographic Conditions

5.1.1 The following general operating parameters are used on gas chromatographs to perform this method utilizing megabore (0.53 or 0.45mm) columns:

Carrier gas:	helium
Column flow:	8 mL/min
Make-up gas:	argon/methane (95%/5% High Purity grade)
Make-up flow:	70 mL/min
Injector:	Grob-type, splitless
Injector temperature:	205°C
Injection:	splitless
Injection volume:	2µL (split - 1 µL per column)
Initial temperature:	150°C
Initial hold time:	0.5 min
Temperature ramp:	4°C per min
Final temperature:	275°C
Final hold time:	9 min
EC detector temperature:	350°C

These GC conditions should be optimized for analyte separation and sensitivity with a particular pair of columns and detectors. Once optimized, the same conditions must be used for the analysis of all standards, samples, blanks and spikes.

5.2 Sample Analysis

5.2.1 Analysis sequence

5.2.1.1 See Appendix II for a detailed analysis injection sequence.

5.2.2 Compound Identification

5.2.2.1 Compounds are tentatively identified if a peak elutes in the retention time window characteristic of that compound on the column 1. To confirm the presence of that compound in the sample extract, the peak must also elute in its characteristic retention time window on a second column. Retention time windows are established as previously described and the absolute retention times are updated each QC period. Compounds can only be identified if the ICV and CCV criteria previously detailed are strictly adhered to.

5.2.2.2 The experienced analyst's judgment weighs heavily in evaluating chromatograms for compound identification. For instance, the retention times of surrogate compounds

may be outside their expected windows due to sample matrix effects. The analyst may decide to re-adjust the target analyte's retention time windows on an ad hoc basis based on such an observed shift. This can occur only on a sample-specific basis and is used when the analyst examining the data suspects that a retention time shift has occurred. If this is done, it must be fully documented in the case narrative notes.

5.2.2.3 Identification of multicomponent analytes occurs when the retention times and ratios of each of the multicomponent peaks present in the sample match the peaks chosen for the particular multicomponent analyte in the initial calibration. These same conditions must be met on both columns in order to confirm the presence of the multicomponent analyte. The experienced analyst's judgment weighs heavily in evaluating the patterns of multicomponent analytes with regards to weathering and matrix interferences.

5.2.3 Compound Quantitation

Target compound concentrations are calculated using the following equations:

5.2.3.1 Aqueous samples

5.2.3.1.1 The external standard equation, as expressed in SW 846 is:

$$\text{Concentration } (\mu g / L) = \frac{(A_x)(V_t)(D)}{(CF_m)(V_i)(V_s)}$$

where:

A_x = Response for the analyte in the extract, in area or height units.
CF_m = Multi-point average CF
V_i = Volume of extract injected, µL.
D = Dilution factor of extract. The final result of an algebraic multiplication of the ratio of all dilution final volumes to initial volumes. For example, if and extract was diluted 100 µL to 1000 µL and subsequently diluted an additional 100 µL to 1000 µL, the expression would be: (1000/10) * (1000/10) = 100 * 100 = 10,000. If no dilution was made, D = 1.
V_t = Volume of total extract, µL.
V_s = Initial sample size, mL.

The reported concentration for multicomponent analytes calculated is based on an average of the concentrations determined for each of the peaks chosen for calibration.

5.2.3.1.2 To report concentrations in alternate units, apply an appropriate factor:

$$mg/L = \mu g/L * 0.001$$

5.2.3.2 Non-aqueous samples

5.2.3.2.1 The results calculation for non-aqueous samples is very similar to that for aqueous samples. The only difference is the inclusion of a total solids term to calculate the dry weight equivalent of the initial sample size.

$$Conc.(\mu g / kg) = \frac{(A_x)(V_t)(D)}{(CF_m)(V_i)(W)(TS/100)}$$

where:

W = Weight of sample extracted or purged, grams.
TS = Total solids, percent.

The reported concentration for multicomponent analytes is based on an average of the concentrations determined for each of the peaks chosen for calibration.

5.2.4 Sample Dilution

5.2.4.1 If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze. The dilution should be made so that the concentration of the analyte requiring dilution is in the mid to upper calibration range.

6. Reports

6.1 Data Packet Organization

6.1.1 See Appendix III for a check list detailing data packet organization.

6.2 Quality Control Reports

6.2.1 All results for quality control tests are entered into the quality control data base. Printouts of all data entered must be included in the data packet. The routine minimum is a method blank report, a blank spike report, and an MS/MSD report.

6.3 Sample Result Reports

6.3.1 Data Qualifying Flags

6.3.1.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

Code	Definition
U	The analyte of interest was not detected, to the reporting limit indicated.
B	The analyte of interest was detected in the method blank associated with the sample, as well as in the sample itself. The flag is applied without regard to the relative concentrations detected in the blank and sample.
J	The analyte of interest was detected below the practical quantification limit. This value should be regarded as an estimate.
D	The value reported is derived from the analysis of a diluted sample or sample extract.
P	When a dual column /dual detector GC technique is employed, this flag indicates that calculated results from the two determinations differ by more than 25%. If the results from one column is significantly higher (25%) the chromatogram is checked for overlapping peaks, or irregular baseline integration. If no anomalies are discovered, the higher result is reported in order to employ the conservative approach relative to protection of the environment.
E	The value reported is based on a sample or sample extract in which the target analyte concentration exceeded the calibration range. The value reported should be considered an estimate.
C	The target analyte's presence was confirmed by GC/MS.

6.4 Control Chart(s)

6.4.1.1 The recovery values for gamma-BHC, Heptachlor, Aldrin, Aroclor 1260, TCMX, and DCB in the Blank Spike are plotted on control charts.

7. References

1). U.S. EPA Contract Laboratory Program Contract, Exhibit D, Section III, March 1990

2). U.S. EPA SW846 Test Methods for Evaluating Solid Waste, Method 8000B, Gas Chromatography, Revision 2, December 1996.

3). U.S. EPA SW846 Test Methods for Evaluating Solid Waste, Method , Organochlorine Pesticides by Gas Chromatography, Method 8081B, Revision 2A, May 1999 .

4). U.S. EPA SW846 Test Methods for Evaluating Solid Waste, Method , Polychlorinated Biphenyls, (PCBs) by Gas Chromatography, Method 8082A, Revision 1A, May 1999 .

APPENDIX I

Standard Solution Concentrations, µg/L

Compound	STD1	STD2	STD3	STD4	STD5
alpha-BHC	5.0	10.0	20.0	40.0	80.0
beta-BHC	5.0	10.0	20.0	40.0	80.0
delta-BHC	5.0	10.0	20.0	40.0	80.0
gamma-BHC (Lindane)	5.0	10.0	20.0	40.0	80.0
alpha-Chlordane	5.0	10.0	20.0	40.0	80.0
gamma-Chlordane	5.0	10.0	20.0	40.0	80.0
Heptachlor	5.0	10.0	20.0	40.0	80.0
Aldrin	5.0	10.0	20.0	40.0	80.0
Heptachlor epoxide	5.0	10.0	20.0	40.0	80.0
Endosulfan I	5.0	10.0	20.0	40.0	80.0
Dieldrin	10.0	20.0	40.0	80.0	160
4,4'-DDE	10.0	20.0	40.0	80.0	160
Endrin	10.0	20.0	40.0	80.0	160
Endosulfan II	10.0	20.0	40.0	80.0	160
4,4'-DDD	10.0	20.0	40.0	80.0	160
Endosulfan sulfate	10.0	20.0	40.0	80.0	160
4,4'-DDT	10.0	20.0	40.0	80.0	160
Methoxychlor	50.0	100	200	400	800
Endrin aldehyde	10.0	20.0	40.0	80.0	160
Endrin ketone	10.0	20.0	40.0	80.0	160
Isodrin	12.5	25.0	50.0	100	200
Chlordane - technical					1000
Toxaphene			500		
Aroclor-1016	100	250	500	1000	2000
Aroclor-1221			500		
Aroclor-1232			500		
Aroclor-1242			500		
Aroclor-1248			500		
Aroclor-1254			500		
Aroclor-1260	100	250	500	1000	2000
2,4,5,6-tetrachloro-m-xylene	5.0	10.0	20.0	40.0	80.0
Decachlorobiphenyl	10.0	20.0	40.0	80.0	160

Appendix I (Continued)

Calibration Stock Solutions, mg/L

Compound	Mix	Conc
alpha-BHC	A	5.0
beta-BHC	B	5.0
delta-BHC	B	5.0
gamma-BHC (Lindane)	A	5.0
alpha-Chlordane	B	5.0
gamma-Chlordane	B	5.0
Heptachlor	A	5.0
Aldrin	B	5.0
Heptachlor epoxide	B	5.0
Endosulfan I	A	5.0
Dieldrin	A	10.0
4,4'-DDE	B	10.0
Endrin	A	10.0
Endosulfan II	B	10.0
4,4'-DDD	A	10.0
Endosulfan sulfate	B	10.0
4,4'-DDT	A	10.0
Methoxychlor	A	50.0
Endrin aldehyde	B	10.0
Endrin ketone	B	10.0
Isodrin	A	25
Chlordane - technical	TChlor	1000
Toxaphene	Tox	500
Aroclor-1016	AR1660	100
Aroclor-1221	AR1221	100
Aroclor-1232	AR1232	100
Aroclor-1242	AR1242	100
Aroclor-1248	AR1248	100
Aroclor-1254	AR1254	100
Aroclor-1260	AR1660	100

*-The single component pesticides are contained in 2 separate mixes (A and B) when utilizing megabore (0.53 or 0.45mm ID) columns. These same components are combined into 1 mix when utilizing capillary (0.25mm ID) columns.

Breakdown Check Solution (CLP PEM solution), µg/L

Compound	Conc
4,4'-DDT	100
Endrin	50

Surrogate Stock Solution, mg/L

Compound	Conc.
2,4,5,6-tetrachloro-m-xylene	10.0
Decachlorobiphenyl	10.0

APPENDIX II

Analysis Sequence

Injection	Sample
	hexane rinse
1	breakdown check standard (PEM)
2	ICV standard INDAM
3	ICV standard INDBM
4	ICV standard multicomponents(for PCB only analysis - can replace above 3 stds)
5	up to 10 subsequent sample or QC extracts
15	solvent rinse or IBLK (optional - not required)
16	CCV standard INDAM
17	CCV standard INDBM
18	CCV standard multicomponents (for PCB only analysis - can replace above 2 stds)
19	up to 10 subsequent sample or QC extracts
last	CCV standard INDAM
last	CCV standard INDBM
last	CCV standard multicomponents (for PCB only analysis - can replace above 2 stds)

APPENDIX III

Data Packet Order

I. QC SUMMARY

_____ Analysts 'Client' Comment (hard copy and floppy)
_____ Surrogate Recovery Summary Report
_____ Blank Spike Report
_____ MS/MSD Report
_____ Method Blank Summary

II. SAMPLE DATA:

_____ Organic Analysis Data Sheet
_____ Sample Confirmation Worksheet
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

III. STANDARD DATA:

_____ Linearity Report

Linearity Standards:
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

Continuing Calibration Standards:
_____ CCV Report
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

APPENDIX III, continued

Other Standards Used to Support Sample Data and Instrument Blanks

V. Raw QC Data:

_____ Method Blank
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

_____ Blank Spike
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

_____ Matrix Spike
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

_____ Matrix Spike Duplicate
_____ Chromatograms, column 1
_____ Chromatograms, column 2
_____ Chromatographic Report, column 1
_____ Chromatographic Report, column 2

APPENDIX III, continued

V. Bench Sheets

_____ Injection Sequence
_____ Target Method
_____ Extraction Bench Sheets
_____ Miscellaneous Work Sheets. i.e. %TS, SDG summary, calculations, HTVR
_____ Standards Logs

VI. Reject Data:

DO NOT COPY DO NOT PAGINATE

Data not used to support sample results.
All data acquired but rejected on account of QC out of control.
Non-routine standards used to support sample data should be placed at the last of the Standard Data section.

APPENDIX IV

Method 8081B QA Requirements and Corrective Actions:

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	5 calibration stds for linear, 6 stds for quadratic, for all single and multi-components, %RSD ≤20% for each analyte or averaged across all analytes.	5 calibration stds for linear, 6 stds for quadratic, for all single and multi-components, %RSD ≤20% for each analyte or averaged across all analytes.	After performing major instrument maintenance or when persistent difficulties meeting CCV criteria occur.	recalibrate or narrate faults if possible	narrative
Initial Calibration Verification	Must be ±15% D for each analyte or averaged across all analytes.	Must be ±15% D for each analyte or averaged across all analytes.	at start of each new analytical sequence, or daily if RTs shift	rerun with new ICV, instrument maintenance, &/or recalibrate (or narrate if possible)	narrative
Continuing Calibration Verification	Must be ±15% D for each analyte or averaged across all analytes.	Must be ±15% D for each analyte or averaged across all analytes.	Every 10 samples	rerun with new ICV, instrument maintenance, &/or recalibrate (or narrate if possible)	narrative
Breakdown	Endrin and DDT breakdown must be <=15%	Endrin and DDT breakdown must be <=15%	At the beginning of each sequence.	Rerun, instrument maintenance	narrative
Method Blank	Presence of any target analytes must be below MDL	Must be below reporting limit	every analytical batch or 1 per 20 samples	Report quantitated contaminants with a "B" flag, or re-extract if necessary	case narrative and corrective action form if re-extracted
Surrogate Recovery	Limits to be determined by the lab	listed in QC database	every sample	Re-extraction of the sample is required if any surrogate is out of control. All surrogates must be in control in the method blank, otherwise all associated samples must be re-extracted. Where contractually required, all surrogates must be within control limits.	case narrative and corrective action form if re-extracted
Matrix Spike Recovery	Limits not specified	listed in QC database	every analytical batch or 1 per 20 samples	if other QC is in control, narrate; otherwise re-extract	case narrative and corrective action form if re-extracted

MS/MSD RPD	Limits not specified	listed in QC database	every analytical batch or 1 per 20 samples	if other QC is in control, narrate; otherwise re-extract	case narrative and corrective action form if re-extracted
Blank Spike Recovery	Limits not specified	listed in QC database	every analytical batch or 1 per 20 samples	if other QC is in control, narrate; otherwise re-extract	case narrative and corrective action form if re-extracted
Standard Reference Material (SRM) Recovery	none required	none required	only if requested	reanalyze or re-extract and reanalyze SRM	case narrative and corrective action form if re-extracted

APPENDIX V

Compound Elution order on DB5 and DB608 Megabore (0.45 or 0.53 mm ID) Columns

DB5	DB608
Tetrachloro-m-xylene	Tetrachloro-m-xylene
alpha-BHC	alpha-BHC
beta-BHC	gamma-BHC (Lindane)
gamma-BHC (Lindane)	beta-BHC
delta-BHC	Heptachlor
Heptachlor	delta-BHC
Aldrin	Aldrin
Isodrin	Isodrin
Heptachlor epoxide	Heptachlor epoxide
gamma-Chlordane	gamma-Chlordane
Endosulfan I	alpha-Chlordane
alpha-Chlordane	Endosulfan I
4,4'-DDE	4,4'-DDE
Dieldrin	Dieldrin
Endrin	Endrin
Endosulfan II	4,4'-DDD
4,4'-DDD	Endosulfan II
Endrin aldehyde	4,4'-DDT
Endosulfan sulfate	Endrin aldehyde
4,4'-DDT	Endosulfan sulfate
Endrin ketone	Methoxychlor
Methoxychlor	Endrin ketone
Decachlorobiphenyl	Decachlorobiphenyl

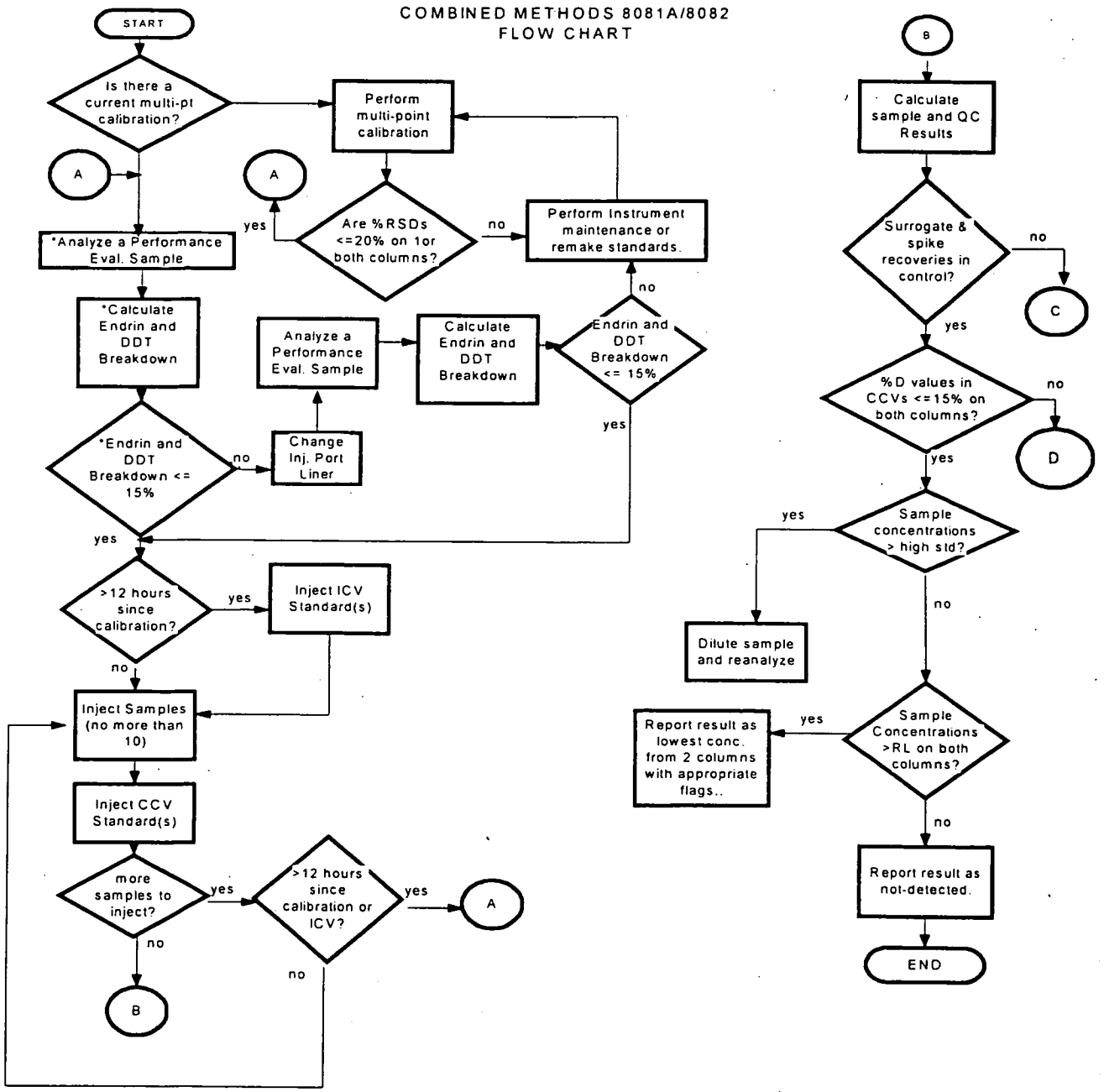
APPENDIX VI

Compound Elution order on DBXLB and DB17ms Capillary (0.25 mm ID) Columns

DBXLB	DB17ms
Tetrachloro-m-xylene	Tetrachloro-m-xylene
alpha-BHC	alpha-BHC
gamma-BHC (Lindane)	gamma-BHC (Lindane)
beta-BHC	beta-BHC
delta-BHC	Heptachlor
Heptachlor	delta-BHC
Aldrin	Aldrin
Isodrin	Isodrin
Heptachlor epoxide	Heptachlor epoxide
gamma-Chlordane	gamma-Chlordane
alpha-Chlordane	alpha-Chlordane
Endosulfan I	Endosulfan I
4,4'-DDE	4,4'-DDE
Dieldrin	Dieldrin
Endrin	Endrin
4,4'-DDD	4,4'-DDD
Endosulfan II	Endosulfan II
Endrin aldehyde	4,4'-DDT
4,4'-DDT	Endrin aldehyde
Endosulfan sulfate	Endosulfan sulfate
Methoxychlor	Methoxychlor
Endrin ketone	Endrin ketone
Decachlorobiphenyl	Decachlorobiphenyl

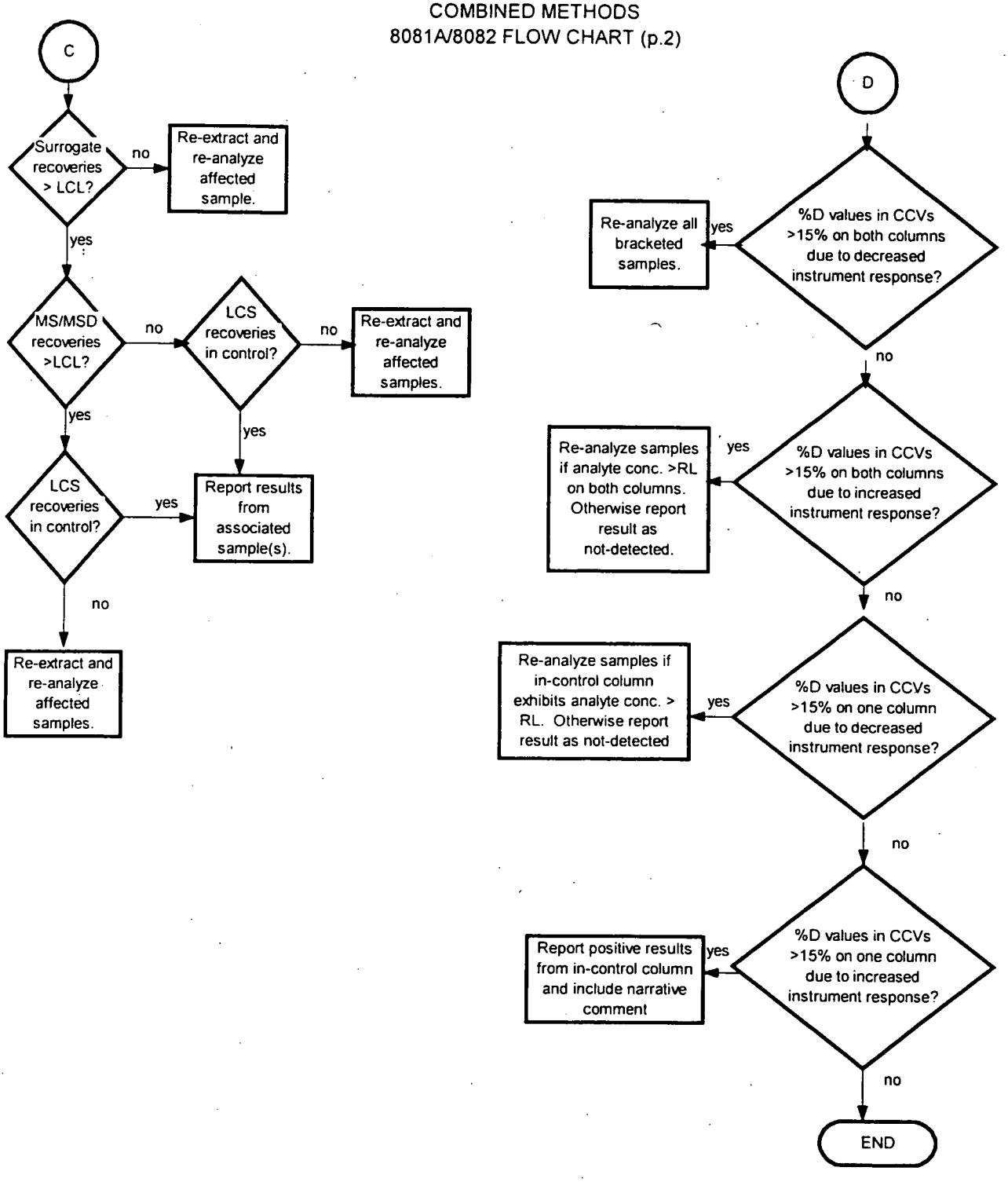
APPENDIX VII

Flow Chart



*These steps can be eliminated if analyzing for SW8082 compounds only

COMBINED METHODS
8081A/8082 FLOW CHART (p.2)



LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8151

Title: **Analysis of Chlorinated Herbicides by Method 8151A**

Revision history:

Number	Date
0	10/08/97
1	2/5/98
2	12/07/98

UNCONTROLLED

Revised by: Monica Carr, Organic Division Manager Date: 12/9/98

Reviewed by: Harry Romberg, QA Officer Date: 12-9-98

Approved by: Kathy Kreps, Laboratory Director Date: 12-8-98

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method describes the procedures and specifications for instrumental analysis of various chlorinated herbicides in water and soil per Method 8151A in SW-846 utilizing capillary columns. Analysis is performed by gas chromatography using a single injection port and splitting into dual GC columns with electron-capture detectors. This system provides quantitation and confirmation of herbicides from a single injection. Dinoseb generally yields poor recoveries using this analysis due to difficulty in bringing the analyte through the extraction procedure. While this is still the case, dinoseb results should be regarded as *estimates*. The following table lists the compounds that may be determined by this method:

ABBREVIATION	COMPOUND NAME
2,4-D	2,4-Dichlorophenoxyacetic acid
2,4-DB	4-(2,4-Dichlorophenoxy) butyric acid
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
2,4,5-TP (Silvex)	2-(2,4,5-Trichlorophenoxy) propionic acid
Dalapon	2,2-Dichloropropionic acid
Dicamba	2-Methoxy-3,6-dichlorobenzoic acid
Dichloroprop (2,4-DP)	2-(2,4-Dichlorophenoxy) propionic acid
Dinoseb	2-(sec-Butyl)-4,6-dinitrophenol
MCPA	(4-Chloro-2-methylphenoxy) acetic acid
MCPP	2,4-(Chloro-2-methylphenoxy) propionic acid
4-Nitrophenol	4-Nitrophenol
Pentachlorophenol	2,3,4,5,6-Pentachlorophenol
Picloram	4-Amino-3,5,6-trichloropicolinic acid

ADDITIONAL COMPOUND
Hexachlorophene

1.1.2 This method is restricted to use by, or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of chromatograms. Each analyst performing this method must have demonstrated the ability to perform the described chromatographic analysis and/or data interpretation.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1 Samples are normally collected in glass containers with Teflon-lined caps. All samples and sample extracts are stored at 4°C. Water samples must be extracted within 7 days of sample collection, soil samples within 14 days of sample collection. All extracts must be analyzed with 40 days of sample extraction.

1.3 Definition of Terms

1.3.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

Batch Identifier	A number given to each preparation or analysis group which uniquely identifies that batch. This number is generally the blank ID for preparation batches and either a sequence number for organic analyses or an analysis number which is similar to the blank ID, only preceded by an "A" rather than a "B" for inorganic batches. The preparation batch IDs are discussed in other documentation.
Blank spike	A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts of target analytes and surrogates are added each time sample extracts are prepared. Blank spikes are required on all HAZWRAP and NEESA work. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard.
CCV	Continuing calibration verification. This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency during the analysis sequence to verify that the instrument has remained in calibration.
CF	Calibration factor. The ratio of analyte instrument response to nanograms injected. This term is defined in the same way in both the CLP contract and SW 846.
CLP	Contract Laboratory Program. The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In the context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.
Corr Coef, CC	Correlation coefficient. A measure of the "goodness of fit" of a set of data to a regression model. The closer the value is to 1, the higher the degree of confidence in the correlation.

DIW	Deionized water. Lab reagent water. Organic-free water. Since the systems used to provide DIW at Laucks all contain carbon polishing filters, they are capable of providing organic-free water for use in method blanks and method blank spikes.
IBLK	Instrument blank. This term is borrowed from CLP. Blank solvent containing the method surrogates is injected into the instrument to monitor for carry over between sample extract injections.
ICV	Initial calibration verification. This term is borrowed from the CLP GC/MS protocol. It is a standard which is injected at the start of each QC period that is compared to the initial multi-point calibration to determine whether the instrument is still in calibration.
IDL	Instrument detection limit. The lowest concentration of a target analyte that will yield a signal:noise ratio of at least 3x. Used as a starting point for selecting MDL study spiking levels.
MDL	Method detection limit. The lowest concentration in a sample which will yield a positive result that is greater than zero at a known level of confidence. MDLs are empirically determined by Laucks.
MDL standard	Method detection limit standard. A standard prepared so that the concentrations of the target analytes are in the range of 1x to 4x the empirically determined MDLs on an extract/digest basis. This standard is used to verify that the instrument is capable of detecting the target analytes on an ongoing basis.
PQL or Reporting Limit	Practical Quantitation Limit or Reporting Limit- The value used when reporting a non-detect. It may be administratively, empirically or contractually set.
QC check standard	Quality control check standard. Referred to in this SOP as a blank spike. A QC check standard is a requirement of SW 846 method 8000 and is used to determine whether the analytical system is in control if MS/MSD recoveries are out of control. See also blank spike.

QC period	Quality control period. An analysis sequence initiated by the analysis of one or more standards, followed by sample extracts/digests, and terminated with a standard analysis. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP.
RRF	Relative Response Factor. A measure of the relative response of an analyte compared to its internal standard. Relative response factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples. RRF is determined by the following equation: $$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$ Where A = area of response measured C = concentration is = internal standard x = analyte of interest
RSD or %RSD	Relative standard deviation or percent relative standard deviation. The ratio of the standard deviation of a set of values to the mean of the set of values expressed as a percentage. A measure of the similarity of the values one to another.
RT, Retention time	The time (in minutes) at which a target analyte elutes from a chromatography column.
RT window	Retention time window. The +/- value which is applied to the ICV to establish the time range used to make tentative compound identifications.
Sequence	A set of sample extracts/digests and standard solutions introduced into an instrument in a chronologically continuous group. See also QC period.

2. Equipment List and Standards

2.1 Chromatographic System

2.1.1 This analysis requires a gas chromatograph with a programmable oven, heated injection port, dual electron-capture detectors, autosampler and an electronic data-acquisition system.

2.1.2 **Equipment list:**
Gas chromatograph: Hewlett-Packard 5890 or equivalent.
Autosampler: Hewlett-Packard 7673 or equivalent.
Electron-capture detectors: Hewlett-Packard or equivalent.
Capillary chromatographic columns of dissimilar phase: J&W DB5 and DB608 or DB17, 30m x 0.45mm, 0.53mm, or 0.25mm megabore or equivalent.
Helium carrier gas and 5% methane/95% argon detector make-up gas

2.2 Standards

2.2.1 Stock standards of all target analytes and surrogates are prepared in methanol from neat materials, using the methyl ester of the compound when it is available or gravimetrically corrected to the acid form. Alternatively, commercially prepared and certified standard solutions can be used, if available. Our main source of neat materials is Chem Service, West Chester, PA. Suppliers may change without notice or immediate update to this Standard Operating Procedure. Neat materials and certified standard solutions are replaced by the manufacturer's expiration date. Refer to Laucks' SOP on the tracebility, documentation, and preparation standards.

2.2.2 Working standards are prepared in hexane from these stocks. Those which are prepared in the free acid form (not prepared from methyl esters) are methylated by derivatization using diazomethane. At this stage all working standards are in methyl ester or ether form. They must be replaced after one year or by the expiration date of the material they were made from, whichever is earlier.

2.2.3 Calibration standards are prepared by combining the stock standards and diluting with hexane to prepare the calibration standard (HERB5) which defines the upper response range of the ECD . The lower levels are diluted by factors of 2, 5, 10, and 20. All calibration standards must be replaced after 6 months or by the expiration date of the material they were made from, whichever is earlier.

2.2.4 Appendix I details the compounds and concentrations contained in all solutions.

3. Safety precautions and Waste Disposal

3.1 Routine Safety Precautions

3.1.1 All standards and sample extracts should be handled as if they contain hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.4 Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.5 The electron-capture detectors used in this analysis contain a radioactive source and should not be opened or otherwise tampered with. Ensure that all gas cylinders are either fastened to an immovable object or capped securely at all times.

3.2 Waste disposal

3.2.1 Solvent wastes generated in using this procedure (expired standards, old sample extracts, rinsates, etc.) should be emptied into the solvent waste container in the fume hood.

3.2.2 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

4. Calibration and Quality Control

4.1 QA Requirements and Corrective Action

4.1.1 Detailed in the following sections are applicable QA requirements and subsequent corrective actions to be applied to this analysis. A summary of these requirements can be found in Appendix IV.

4.2 Method Detection Limit Study

4.2.1 Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in the Laucks SOP on MDL Studies. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration near the anticipated method detection limit. A Student's T-test is then applied to these

measured values to calculate the MDL. Current MDLs are listed in the quality control database.

4.3 Method Validation

4.3.1 Prior to the analysis of any samples, it is necessary to validate the method. A method validation study is performed in a similar manner to an MDL study with the exception that a minimum of 4 replicates are required and the concentration levels must be similar to those found in SW-846.

4.3.2 The results must be equal to or better than the spike recoveries tabulated in SW 846. These criteria and recommended spiking concentrations for method validation are tabulated in SW 846.

4.4 Retention Time Windows

4.4.1 Prior to the analysis of any samples, it is necessary to establish retention times windows for the method by analyzing standards for all target analytes over at least a 72-hour period. This need not be a single 72 hour sequence but can be 3 chronologically contiguous sequences. These standards should be inter-mixed with real sample extracts in order to mimic actual instrument operating conditions. Tabulate the retention times for all standard compounds and compute the standard deviations of all the retention times. Retention time normalization techniques may be applied if appropriate. For megabore capillary columns, a default RT window of ± 0.05 minutes may be used. Details of the procedure for determining retention time windows can be found in Laucks SOP on establishing retention time windows.

4.5 Initial Multi-Point Calibration

4.5.1 Analyze standard solutions using at least 5 different concentration levels. The lowest concentration should be at a concentration near, but above, the method detection limit. The highest concentration should be below the upper usable working limit of the detector. Inject the standard solutions from the lowest concentration to the highest. The currently used calibration concentrations are listed in Appendix I.

4.6 External Standard Calibration

4.6.1 External standard initial calibration data is evaluated by determining the %RSD of the calibration factors.

4.6.2 CFs are calculated using the equation:

$$CF = \frac{\text{response}}{\text{ng injected}}$$

4.6.3 The calculated CFs are tabulated and the %RSD calculated. If the %RSD for the Cfs is ≤ 20% over the calibration range, then linearity through the origin may be assumed, and the average CF may be used to determine sample concentrations.

4.6.4 Corrective action

4.6.4.1 If the criteria are not met, the instrument operating conditions must be checked.

4.6.4.2 If the problem appears to be associated with a single standard, that one standard may be reanalyzed and the RSD recalculated. Replacing the standard may be necessary.

4.6.4.3 A third alternative is to narrow the calibration range.

4.6.4.4 However, the initial calibration may still be met if the following conditions are met:

4.6.4.4.1 The mean of the RSD values for all analytes in the calibration is less than or equal to 20%.

4.6.4.4.2 The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project.

4.6.4.4.3 The data must be submitted with a summary of the initial calibration data, or a specific list of those compounds which exceed the 20% RSD, and the results of the mean RSD calculation.

4.7 Initial Calibration Verification

4.7.1 Concentration and/or CF Criteria

4.7.1.1 At the beginning of an analysis sequence analyze a mid-range calibration standard. The computed calibration factor (CF) or concentration measurement must meet the criteria detailed below.

4.7.1.2 Using the appropriate calculation technique (average CF, linear calibration, or non-linear calibration, or internal calibration) compute either CFs or concentration values. For linear calibrations the ICV standard can be verified by calculating either the percent difference of the percent drift. For non-linear calibrations the ICV standard can be verified by calculating the percent difference.

4.7.1.2.1 The percent difference calculation compares the ICV CFs to the mean CFs from the initial multi-point calibration. The percent difference is calculated as follows:

$$\%D = \frac{Cv - \overline{CF}}{\overline{CF}} \times 100$$

where:

C_v = Calibration Factor

$\overline{CF}$ = Mean Calibration Factor

4.7.1.2.2 The percent drift calculation compares the ICV calculated concentrations to the theoretical (or actual) concentration of the ICV standard. The percent drift is calculated as follows:

$$\%D = \frac{C_c - C_T}{C_T} \times 100$$

where:

C_c= Calculated Concentration
C_T = Theoretical Concentration

4.7.2 If the response (or calculated concentration) for an analyte is ±15% of the response obtained during the initial calibration, then the initial calibration is considered still valid. Alternatively, if the average of the responses for all analytes is within 15%, then the calibration has been verfied. However, the average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project, and the data must be provided with the calibration verification data.

4.7.3 Corrective action

4.7.3.1 If the ICV criteria are not met, perform system maintenance and renalyze the verfication standard. If the criteria still cannot be met, the system must be recalibrated.

4.8 Updating Retention Time Windows

4.8.1 The retention time windows for compound identification are updated using the retention times for each target analyte in the ICV standard as the center of the window and the previously determined retention time window half-width to establish the retention time range to be used for compound identification.

4.9 Continuing Calibration Verification

4.9.1 A mid-range calibration standard is analyzed at the frequency of every 10 samples. In addition, this standard must be the last injection made in the analysis sequence.

4.9.2 Criteria

4.9.2.1 After every 10 sample extract injections, a CCV standard is analyzed. The CF or concentration for each analyte is calculated and the percent difference or percent drift is calculated as shown above.

4.9.3 If the response (or calculated concentration) for an analyte is ±15% of the response obtained during the initial calibration, then the initial calibration is considered still valid. Alternatively, if the average of the responses for all analytes is within 15%, then the calibration has been verfied. However, the average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project, and the data must be provided with the calibration verification data.

4.9.3.1 The retention times for all target analytes must fall within the RT windows established by the ICV.

4.9.4 Corrective action

4.9.4.1 Check calculations or perform instrument maintenance. To validate the quantification of target analytes in analytical samples, the samples must be bracketed by in-control CCVs. All samples bracketed by an out of control CCV must be reanalyzed unless the CCV demonstrates an increase in response and no analytes are detected above the RL in the associated samples.

4.10 Method Blanks

4.10.1 Criteria

4.10.1.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples extracted at the same time or one blank every 20 samples which ever is more frequent. Any analyte response above the detection limit is reported. Method blank control limits are detailed in the quality control database (QC_DB).

4.10.2 Corrective action

4.10.2.1 Corrective action may necessitate re-extraction of the sample set. For example if an analyte were found in the blank but not in any of the associated samples then the sample group may not require re-extraction. In any event it is the laboratory's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the chromatograms be minimized. In the extreme case of chronic contamination, blanks may have to be analyzed from each stage of the sample processing to determine the contamination source so it can be eliminated. In all cases where blank contamination exceeds the control limit a narrative comment must be made which documents the corrective actions taken.

4.11 Method Blank Spikes

4.11.1 Criteria

4.11.1.1 A method blank spike follows the same protocol as with the matrix spike analysis except that the spiking solution is added to a method blank solution instead of an actual sample. A method blank with added analytes is a method blank spike. A method blank spike is similar to a QC check standard. Method blank spike recoveries must meet the criteria specified in the quality control database (QC_DB).

4.11.2 Corrective action

4.11.2.1 The method blank spike is used to determine whether a method is in control during sample preparation and analysis. Sample re- extraction and re-analysis would be triggered by an out of control method blank spike only if the sample surrogate recoveries and MS/MSD spike recoveries indicated sample processing errors.

4.12 Matrix Spike

4.12.1 Criteria

4.12.1.1 A sample is chosen at random from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to extraction. It is required that a matrix spike analysis be performed with each extraction batch. The minimum frequency for MS analysis is 1 each per 20 samples per matrix. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$\%\,\text{recovery} = \frac{SS - S}{SA} \times 100$$

where:

SS = spiked sample result
S = unspiked sample result
SA = amount spiked

4.12.1.2 The recovery criteria are detailed in the QC database (QC_DB). In the instance that the native target analyte concentration is greater than 5x the spike added concentration, the MS recovery control limits do not apply. In this case, treat the MS/MSD pair as duplicates and report them as such in the quality control database.

4.12.2 Corrective action

4.12.2.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action may involve recalculation, re-extraction, and/or reanalysis. This process should also look at the recovery of surrogate compounds in the MS sample and at the recovery of matrix spiking compounds from the extraction batch blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.13 Matrix Spike Duplicate

4.13.1 Criteria

4.13.1.1 The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values.

4.13.1.2 This calculation is as follows:

$$\% RPD = \frac{|S_1 - S_2|}{(S_1 + S_2)/2} \times 100$$

where:

S_1 = measured concentration for MS sample
S_2 = measured concentration for MSD sample

4.13.1.3 RPD control limits are detailed in the QC database (QC_DB).

4.13.2 Corrective action

4.13.2.1 If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility.

4.14 Surrogate Recovery

4.14.1 Criteria

4.14.1.1 Surrogates are chemically similar compounds added to every sample, method blank, and QC sample prior to sample processing. They are used to monitor for potential sample processing errors and matrix effects. Surrogate compound recoveries are calculated as follows:

$$\% \text{ recovery} = \frac{S_m \times 100}{S_a}$$

where:

S_m = concentration of surrogate measured in extract
S_a = concentration of surrogate added

4.14.1.2 Detailed surrogate recovery control limits are tabulated in the laboratory QC database (QC_DB).

4.14.2 Corrective Action

4.14.2.1 Check calculations for possible error. Low surrogate recoveries are greater potential indicators of poor method performance than high surrogate recovery since non-GC/MS methods cannot separate co-eluting interferences. Hence corrective action is not usually required for high surrogate recoveries. These cases should be evaluated for other possible causes (such as double surrogate spiking or incorrect dilution factors).

4.14.2.2 Low surrogate recoveries in the method blank may require that all the samples in the associated batch be re-extracted and re-analyzed. In any case, it is imperative to identify the problem associated with low recovery so that it can be corrected. It is a requirement that all out of control surrogate recoveries and the corrective action taken be discussed in the narrative.

5. Operation procedures

5.1 Chromatographic Conditions

5.1.1 The following are typical operating parameters used to perform this method. There may be times when adjustments are made in order to optimize the analysis.

Column flow	7-8 mL/min
Make-up gas	argon/methane (95%/5% High Purity Grade)
Make-up flow	70 mL/min
Injector	grob-type, split/splitless with 4mm wide bore deactivated liner
Injector temperature	205°C
Injection	on-column
Injection volume	1µl per column (2µl total)
Initial temperature	45°C
Initial hold time	1.0 min
Temperature ramp	25°C per min to 150°C
Hold time	1.0 min
Temperature ramp	5°C per min to 240°C
Hold time	0 min
Temperature ramp	25°C per min to 290°C
Final hold time	0 min
EC detectors temperature	325°C

5.2 Sample Analysis

5.2.1 Analysis sequence

5.2.1.1 See Appendix II for a detailed analysis injection sequence.

5.2.2 Compound Identification

5.2.2.1 Compounds are tentatively identified if a peak elutes in the retention time window characteristic of that compound on the primary column. To confirm the presence of that compound in the sample extract, the peak must also elute in its characteristic retention time window on a second column. Retention time windows are established as previously described and are updated if retention times of the ICV have shifted outside existing windows. Compounds can only be identified if the ICV and CCV criteria previously detailed are strictly adhered to.

5.2.2.2 The experienced analyst's judgment weighs heavily in evaluating chromatograms for compound identification. For instance, the retention times of surrogate compounds may be outside their expected windows due to sample matrix effects. The analyst may decide to re-adjust the target analyte's retention time windows on an ad hoc basis based on such an observed shift This can occur only on a sample-specific basis and is used when the analyst examining the data suspects that a retention time shift has occurred. If this is done,

examining the data suspects that a retention time shift has occurred. If this is done, it must be fully documented in the case narrative notes. If the concentration of any target analyte exceeds the calibration range, the sample extract must be diluted and reanalyzed.

5.2.3 Compound Quantitation

Target compound concentrations are calculated using the following equations:

5.2.3.1 Aqueous samples

The external standard equation, as expressed in SW 846 is:

$$\text{Concentration } (\mu g / L) = \frac{As \times Vt \times D}{\overline{CF} \times Vi \times Vs}$$

where:

A_S = Area or height of the peak for the analyte in the sample.
V_i = Volume of extract injected, µL.
D = Dilution factor of extract. The final result of an algebraic multiplication of the ratio of all dilution final volumes to initial volumes. For example, if and extract was diluted 10 µL to 1000 µL and subsequently diluted an additional 10 µL to 1000 µL, the expression would be: (1000/10) * (1000/10) = 100 * 100 = 10,000.
If no dilution was made, D = 1.
V_t = Volume of total extract, µL.
V_S = Initial sample size, mL.
$\overline{CF}$ = Mean calibration factor.

To report concentrations in alternate units, apply an appropriate factor:

mg/L = µg/L * 0.001

5.2.3.2 Non-aqueous samples

The results calculation for non-aqueous samples is very similar to that for aqueous samples. The only difference is the inclusion of a total solids term to calculate the dry weight equivalent of the initial sample size.

$$Conc.(\mu g / kg) = \frac{Vt \times As \times D}{CF \times Vi \times Ws}$$

where:

Ws = Weight of sample extracted or purged, grams. Either the wet weight or dry weight..

6. Reports

6.1 Data Packet Organization

See Appendix III for a check list detailing data packet organization.

6.2 Quality Control Reports

All results for quality control tests are entered into the lab quality control data base. Printouts of all data entered must be included in the data packet. The routine minimum is a method blank report, a method blank spike report, and an MS/MSD report.

6.3 Sample Result Reports

6.3.1 Data Qualifying Flags

Sample report results are qualified with data qualifying flags. These flags have the following definitions:

Code	Definition
U	The analyte of interest was not detected, to the reporting limit indicated.
B	The analyte of interest was detected in the method blank associated with the sample, as well as in the sample itself. The B flag is applied without regard to the relative concentrations detected in the blank and sample.
J	The analyte of interest was detected below the practical quantification limit. This value should be regarded as an estimate.
D	The value reported is derived from the analysis of a diluted sample or sample extract.
P	When a dual column /dual detector GC technique is employed, this flag indicates that calculated results from the two determinations differ by more than 25%. Generally, we report the lower value.
E	The value reported is based on a sample or sample extract in which the target analyte concentration exceeded the calibration range. The value reported should be considered an estimate.
C	The target analyte's presence was confirmed by GC/MS.

7. References

1) *SW846 Test Methods for Evaluating Solid Waste*, Method 8000B Gas Chromatography, US EPA Office of Solid Waste and Emergency Response, Revision 2, December 1996.

2) *SW846 Test Methods for Evaluating Solid Waste*, Method 8151A Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization, US EPA Office of Solid Waste and Emergency Response, Revision 1, December 1996.

APPENDIX I

Standard Solution Concentrations, ng/mL (Acid Form)

Compound	STD1	STD2	STD3	STD4	STD5
2,4-D	4.6	23	46	92	161
2,4-DB	92.	23	46	92	161
2,4,5-T	4	20	40	80	140
2,4,5-TP (Silvex)	4	20	40	80	140
Dalapon	4	20	40	80	140
Dicamba	4	20	40	80	140
Dichloroprop (2,4-DP)	4.6	23	46	92	161
Dinoseb	4	20	40	80	140
MCPA	2000	5000	10000	20000	35000
MCPP	3500	7500	10000	20000	35000
4-Nitrophenol	10	50	100	200	350
Pentachlorophenol	1	5	10	20	35
Picloroam	4	20	40	80	140
DCBA(surr)	10	50	100	200	350
DCPPA (surr)	10	50	100	200	350
Hexachlorophene	1	5	10	20	35

At the time of this writing these are the current calibration concentration levels. However, these levels may change due to project-specific requirements, or a change in standard suppliers.

APPENDIX II

Analysis Sequence

Injection	Sample
	rinse
1	ICV standard HERB3
2	up to 10 subsequent sample or QC extracts
12	CCV standard HERB3
13	up to 10 subsequent sample or QC extracts
last	CCV standard HERB3

APPENDIX III

Data Packet Sequence

I. QC SUMMARY

Surrogate Recovery Summary Report
Blank Spike Report
MS/MSD Report
Method Blank Summary

II. SAMPLE DATA:

Organic Analysis Data Sheet
Sample Confirmation Worksheet
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column

III. STANDARD DATA:

Initial Calibration Verification
Linearity Report
Surrogate RT Evaluation Report
CCV Reports
Confirmation Reports

Linearity Standards:
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column

Continuing Calibration Standards:
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column
Other Standards Used to Support Sample Data and Instrument Blanks

V. Raw QC Data:

Method Blank
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column

Blank Spike
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column

Matrix Spike
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column

Matrix Spike Duplicate
Chromatograms, primary column
Chromatograms, secondary column
Chromatographic Report, primary column
Chromatographic Report, secondary column

V. Bench Sheets

Injection Sequence
Extraction Bench Sheets
Miscellaneous Work Sheets. i.e. %TS, SDG summary, calculations, HTVR
Standards Logs

VI. Reject Data:

Data not used to support sample results.
All data acquired but rejected on account of QC out of control.
Non-routine standards used to support sample data should be placed at the last of the Standard Data section.

APPENDIX IV

Method 8151 QA Requirements and Corrective Actions:

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	5 calibration standards, bracketing linear range RPD ≤20% (or average of RPDs ≤20%).	5 calibration standards, RPD ≤ 20% for analytes (or average of RPDs ≤20%).	once per analytical sequence	recalibrate or narrate faults if possible	narrative
Initial Calibration Verification	Must be ±15% D for all quantitated analytes (or average of %Ds ±15%).	Must be ±15% D for all quantitated analytes (or average of %Ds ±15%).	once per daily analytical sequence	rerun with new ICV, instrument maintenance, &/or recalibrate (or narrate if possible)	narrative
Continuing Calibration Verification	Must be ±15% D for all quantitated analytes (or average of %Ds ±15%).	Must be ±15% D for all quantitated analytes (or average of %Ds ±15%).	Every 10 samples	rerun with new ICV, instrument maintenance, &/or recalibrate (or narrate if possible)	narrative
Method Blank	Must be below MDL	Must be below reporting limit	every analytical batch or 1 per 20 samples	Report quantitated contaminants with a "B" flag, or re-extract if necessary	case narrative and corrective action form if reextracted
Surrogate Recovery	Limits to be determined by lab	listed in QC database	every sample	if other QC is in control, narrate; otherwise reextract	case narrative and corrective action form if reextracted
Matrix Spike Recovery	every analytical batch or 1 per 20 samples, limits to be determined by lab	listed in QC database	every analytical batch or 1 per 20 samples	if other QC is in control, narrate; otherwise reextract	case narrative and corrective action form if reextracted
MS/MSD RPD	every analytical batch or 1 per 20 samples, limits to be determined by lab	listed in QC database	every analytical batch or 1 per 20 samples	if other QC is in control, narrate; otherwise reextract	case narrative and corrective action form if reextracted
Blank Spike Recovery	every analytical batch or 1 per 20 samples, limits to be determined by lab	listed in QC database	every analytical batch or 1 per 20 samples	if other QC is in control, narrate; otherwise reextract	case narrative and corrective action form if reextracted
Standard Reference Material (SRM) Recovery	none required	none required	only if requested	reanalyze or reextract and reanalyze SRM	case narrative and corrective action form if reextracted

APPENDIX V

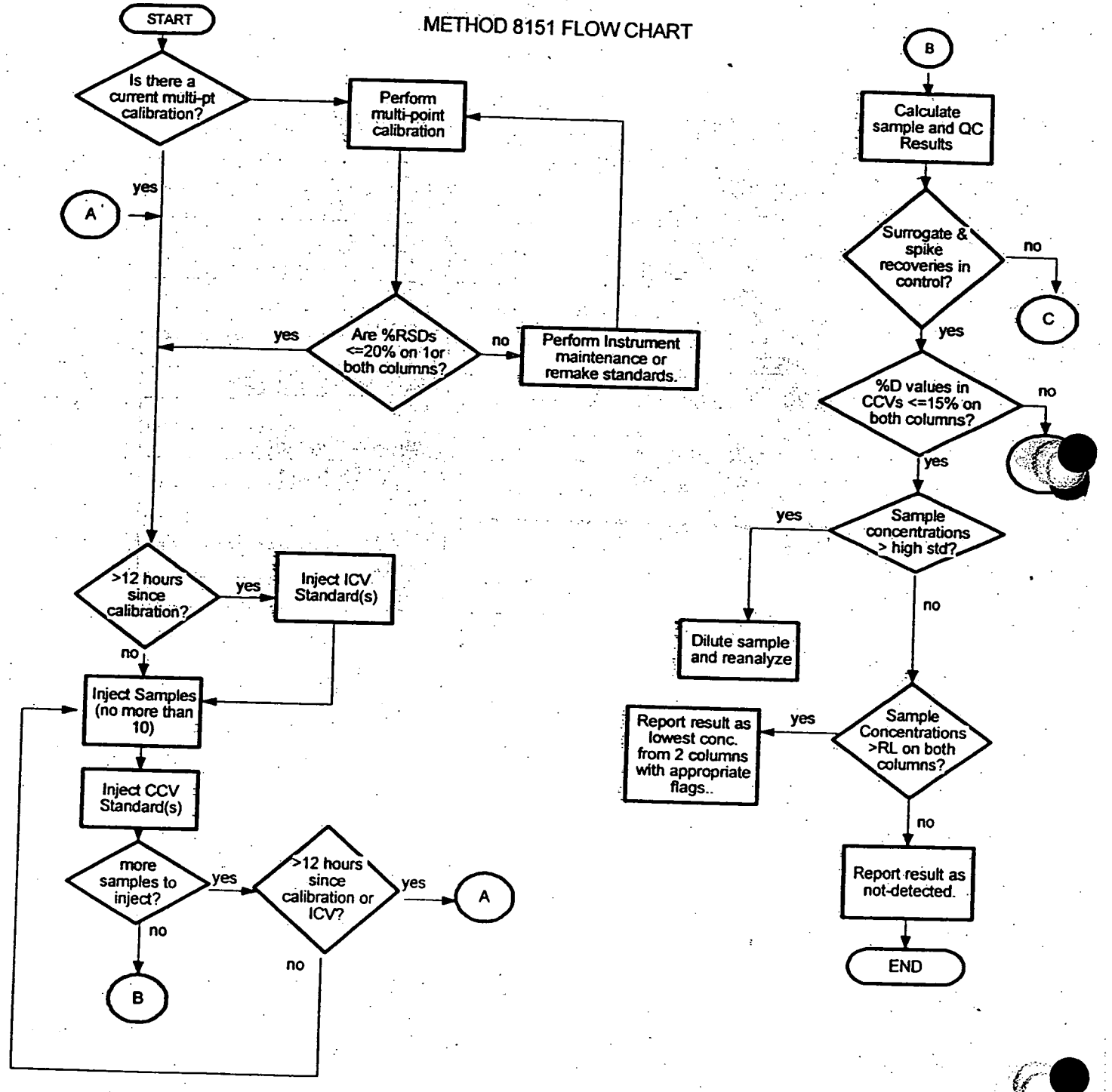
Compound Elution Order

Column DB-5	Column DB-608
Dalapon	Dalapon
2,6-DCBA (surr)	2,6-DCBA (surr)
4-Nitrophenol	4-Nitrophenol
2,4-DCPAA (surr)	2,4-DCPAA (surr)
Dicamba	MCPP
MCPP	Dicamba
MCPA	MCPA
Dichloroprop (2,4-DP)	Dichloroprop (2,4-DP)
2,4-D	2,4-D
Pentachlorophenol	Pentachlorophenol
2,4,5-TP (Silvex)	2,4,5-TP (Silvex)
2,4,5-T	2,4,5-T
2,4-DB	Dinoseb
Dinoseb	2,4-DB
Picloram	Picloram
Hexachlorphene	Hexachlorphene

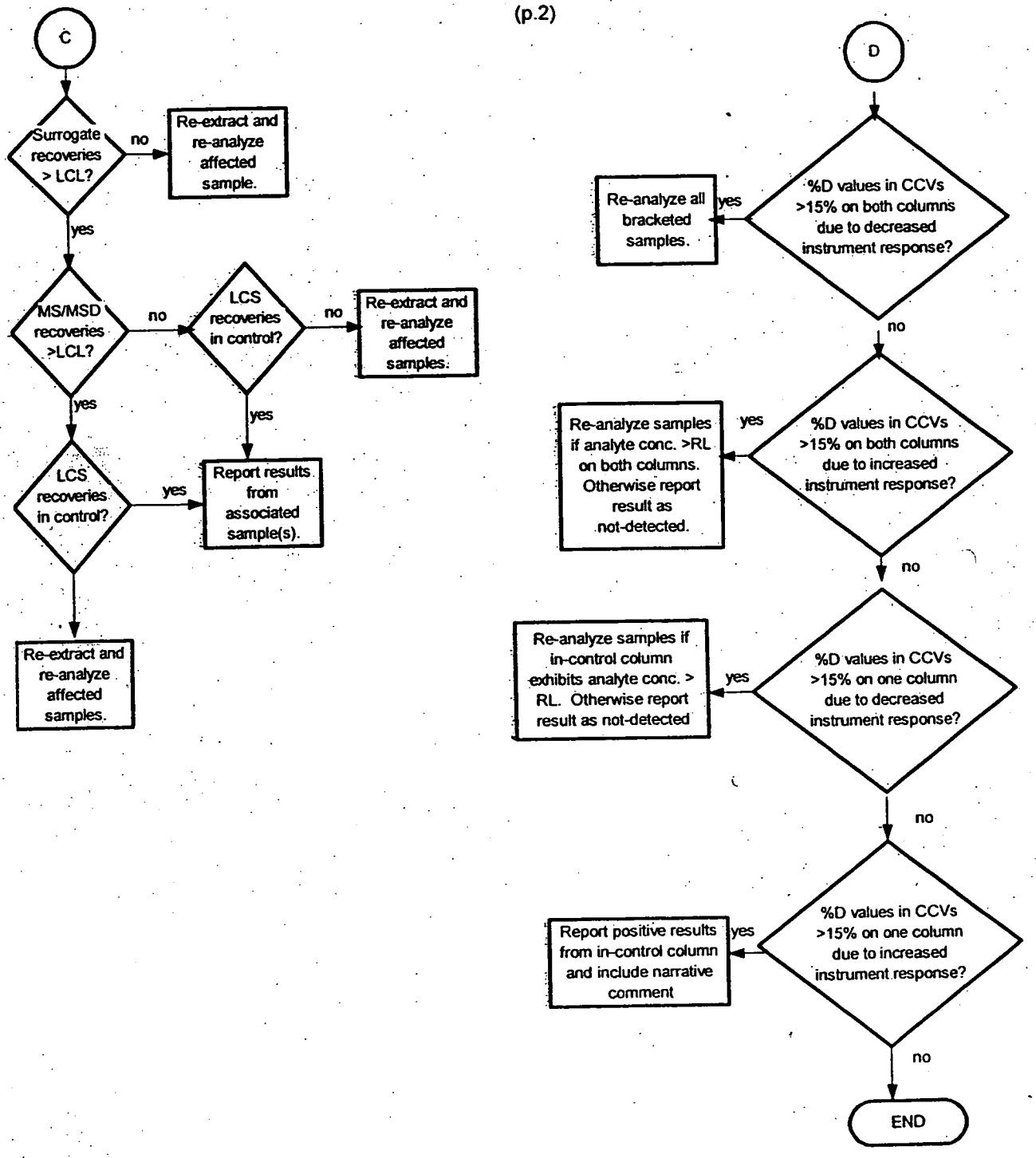
APPENDIX VI

Flow Chart

METHOD 8151 FLOW CHART



METHOD 8151 FLOW CHART
(p.2)



LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8265

Title: **Determination of Volatile Organic Compounds by Method SW 8260B**

Revision history:

Number	Date
0	01/29/98
1	06/17/98
2	04/20/00

Controlled Document

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1. Introduction and Scope

1.1 Method Description

Method 8260 is used in the determination of volatile organic compounds in soil, sediment, aqueous, and other matrices. This SOP addresses the determination of volatile organics in different matrices, which include medium level soils as well as low level water samples. A 25 mL sample volume is employed in order to achieve lower detection limits for the low level waters. In addition, the instrument acquisition parameters have been added for the analysis of vinyl chloride by Selected Ion Monitoring (SIM) in Appendix III, and Appendix IV contains a tabular list of the non-routine Appendix IX analytes and their respective calibration ranges.

1.1.1 Because this method employs sample introduction via a purge and trap sample concentrator, it is applicable to volatile compounds that have boiling points below 200°C and that are insoluble or only slightly soluble in water. Compounds that are more soluble in water have elevated detection limits due to their decreased purging efficiency. These include, but are not limited to ketones, nitriles, acetates, acrylates and ethers.

1.1.2 This method is restricted to use by, or under the supervision of analysts experienced in the use of purge and trap systems, gas chromatography/mass spectroscopy and in the interpretation of chromatograms and mass spectral data. Each analyst performing this method must have demonstrated the ability to perform the described chromatographic analysis and data interpretation.

1.2 Method Deviations

1.2.1 Detailed below are any deviations from the published version of method SW 8260B. All deviations are followed as the standard operation procedure by Laucks Testing Labs.

1) Laucks uses 1/2 the reporting limit (low level standard) for method blank criteria instead of method detection limits as referenced in SW 846. Common laboratory solvents, such as methylene chloride and acetone, are allowed to be present in the method blanks at the RL. Refer to Section 6.4 for detailed method blank criteria.

2) The retention time window used for internal standards in all analyses is +/- 0.50 minutes relative to the daily CCV standard. This window is considerably narrower than the 0.06 RRT units specified in method SW 8260B and is considered more likely to ensure acceptable method performance.

3) The BFB tuning criteria used is taken from CLP SOW OLM03.1, which is not a deviation from the method since SW 8260B allows the use of alternative tuning criteria, e.g., CLP and/or 524.2 The tuning criteria are tabulated in section 4.4.5.

1.3 Sample Collection, Sample Storage, Holding Times

1.3.1 Waters

1.3.1.1 Samples are collected with zero headspace in 40 mL glass containers containing preservative (either HCl, H_2SO_4 or solid $NaHSO_4$) and sealed with Teflon-lined caps.

1.3.1.2 The water samples are preserved to a pH of ≤2, and all samples are stored at 4°C.

1.3.1.3 The holding time to analysis is 14 days from date of collection. The pH values for the water samples are measured subsequent to sample analysis. The pH values, when not preserved to a pH ≤2 are noted in the instrument logbook and the client report.

1.3.2 Soils

1.3.2.1 At the time of this writing, the 3rd update of the 3rd edition to SW 846 requires that low level soils be collected in duplicate using 5 gram and/or 1 gram aliquots which are to be weighed out in the field. The soil samples are to be collected in a 40 mL vial containing water, sodium bisulfate, and a stir bar. 0.2 grams of sodium bisulfate are added for each 1 gram of soil. Therefore, when collecting 5 grams of sample, the VOA vial should contain 1 gram of sodium bisulfate. The sodium bisulfate is added in order to ensure a sample pH of ≤2. The vials used for low level soils should have the tared weight recorded on the label and sealed with septum-lined screw caps.

1.3.2.2 Another option is the use of the EnCore™ sampler, the Purge-and-Trap Sampler™, and a cut plastic syringe to transfer the sample to the soil vial. If the EnCore™ sampler is used in the field, the samples may be stored for up to 48 hours. However, samples collected in this device should be transferred to the soil sample vials (and preserved) as soon as possible, or analyzed within 48 hours. The holding time for soils is 14 days from the date of collection.

1.3.2.3 At the time of this writing, the 3rd update of the 3rd edition to SW 846 requires that high level soils be collected in using one of the following options:

1.3.2.3.1 Option 1: Samples will be collected in duplicate using 5 gram and/or 1 gram aliquots which are to be weighed out in the field. The soil samples are to be collected in a 40 mL vial containing methanol. The vials used for high level soils should have the tared weight recorded on the label and sealed with septum-lined screw caps.

1.3.2.3.2 Option 2: Samples will be collected using an EnCore type sampler or equivalent, and preserved at the laboratory by freezing.

1.3.2.3.3 Option 3: Samples will be collected in vials with zero headspace.

1.3.2.4 The practices in sections 1.3.2.1 and 1.3.2.2 will be implemented as SAPs, QAPs, agencies and clients require without updating this SOP until the practice is routine and this document is up for its annual review. Until this practice is routine and accepted by all agencies Laucks will continue to accept unpreserved soil samples for low or high level analysis. The samples must be collected in 2- or 4-oz glass containers and sealed with teflon-lined caps. These samples will be introduced by method 5030A and analyzed according to this SOP. Please note that for South Carolina samples, Method 5035 must be followed.

1.3.2.5 The holding time to analysis is 14 days from date of collection.

1.4 Definition of Terms

1.4.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

Blank Spike	A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts or target analytes and surrogates are added each time samples are analyzed. Blank spikes are required on all HAZWRAP and NFESC work. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard.
CCC	Calibration check compound. There are 6 analytes which must meet the minimum %RSD of 30% in the initial calibration and a %D of 20% in the continuing calibration standard to validate linearity. These analytes are 1,1-dichloroethane, chloroform, 1,2-dichloropropane, toluene, ethylbenzene and vinyl chloride.

CCV	Continuing calibration verification. This is a standard analyzed at some prescribed frequency during the analysis sequence to determine whether the instrument has remained in calibration.
CLP	Contract Laboratory Program. The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In the context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.
IBLK	Instrument blank. An instrument blank is PFW containing the method surrogates and is introduced into the instrument to monitor for carry over between sample analyses.
IDL	Instrument detection limit. The lowest concentration of a target analyte that will yield a signal:noise ratio of at least 3x. Used as a starting point for selecting MDL study spiking levels.
MDL	Method detection limit. The lowest concentration in a sample which will yield a positive result that is greater than zero at a known level of confidence. MDLs are empirically determined by Laucks.
PFW	Purge-free water. Laboratory deionized water that is boiled for 30 minutes prior to use. The systems used to provide deionized water at Laucks all contain carbon polishing filters which are capable of providing purge-free water for use as reagent water.
QC Check Standard	Quality control check standard. Referred to in this SOP as a blank spike. A QC check standard is a requirement of SW 846 method 8000 and is used to determine whether the analytical system is in control if MS/MSD recoveries are out of control. See also blank spike.
QC Period	Quality control period. An analysis sequence initiated by the injection of BFB, followed by the standard. A QC period is terminated after 12 hours from the injection of BFB.

Reporting Limit (RL)	The reporting limit is defined by the low level standard, also referred to as the practical quantiation limit (PQL).
RF	Response factor. A measure of the response of an analyte compared to its internal standard response. Response factors are determined by standard analysis and are used in the calculation of concentrations of analytes in samples.
RRT	Relative retention time. A measure of the retention time of an analyte compared to the retention time of its internal standard.
RSD or %RSD	Relative standard deviation or percent relative standard deviation. The ratio of the standard deviation of a set of values to the mean of the set of values. A measure of the similarity of the values one to another.
RT	Retention time. The time (in minutes) at which a target analyte elutes from the GC column.
Sequence	A set of samples and standard solutions introduced into an instrument in a chronologically continuous group. See also QC period.
SPCC	System performance check compound. Specified compounds in which the minimum RFs must be met in order to demonstrate that the initial and continuing calibration standards are in control. These compounds are chloromethane, 1,1-dichloroethane, bromoform, chlorobenzene, and 1,1,2,2-tetrachloroethane.

2. Equipment List and Standards

2.1 Chromatographic System

2.1.1 Gas Chromatograph: Hewlett Packard 5890 I or II employing a low-dead-volume interface from the sample concentrator to the GC injection port.

2.1.2 Carrier Gas: Helium 99.995% (high purity grade) or better.

2.1.3 Column: 60m x 0.25mm x 1.4 µm film thickness, or 30 m x 0.53 mm x 3.0 µm film thickness or 75 m x 0.45 x 2.55 µm film thickness, fused silica capillary column (J&W DB-624 or Restek RTx-624 or equivalent).

2.1.4 Purge and Trap: OI Analytical 4460A and 4560 sample concentrators or equivalent.

2.1.5 Autosampler: Dynatech Precision Sampling PTA-30W/S or equivalent.

2.1.6 GC/MS Interface: Hewlett Packard 59913A jet separator assembly or equivalent.

2.1.7 Mass Spectrometer: Hewlett Packard 5970B or equivalent.

2.1.8 Data System: Teknivent.

2.1.9 Trap: OI Corporation, Supelco, or equivalent. Examples are listed below:

1) 1 cm 3% SP-2100/Chromosorb W AW, 7.7 cm Tenax TA, 7.7 cm silica gel 15, 7.7 cm activated charcoal. Supelco Pt No.:2-1139.

2) VOCARB 3000. 10 cm Carbopack C, 6 cm Carboxen 1000, 1 cm Carboxen 1001. Supelco Pt No.: 2-1131.

3) VOCARB 4000. 8.5 cm Carbopack C, 10 cm Carbopack B, 6 cm Carboxen 1000, 1 cm Carboxen 1001. Supelco Pt. No.: 2-1143.

2.1.10 Miscellaneous: Assorted gas-tight calibrated syringes, pipettes, 40 mL vials, caps, septa, sea sand, purge and trap grade methanol, ferrules, pH strips, purge-free DIW, volumetrics, laboratory oven capable of heating glassware up to 100°C, and assorted supplies.

2.2 Standards

2.2.1 Overview of Volatile Standards Preparation

2.2.1.1 All standards are made using a high purity purge and trap grade methanol. Every lot number of methanol is analyzed prior to use to ensure that it is free of volatile organic contaminants. A record of analysis of an aliquot from each batch is stored for a minimum of one year.

2.2.1.2 Two standard logbooks are employed to document all volatile standards. One standard logbook is maintained for stock solutions prepared from neat materials and to record the login of certified standards. The other standard logbook is maintained for working solutions which include solutions procured from commercial sources, as well as those solutions made in the laboratory. All standards are assigned a unique identifier to enable cross-referencing of each individual standard back to the supplier's lot number. In addition, all standards are labeled with the standard concentration, the solvent, date prepared, expiration date, analyst's initials, and the standard reference number. Refer to Laucks' SOP on the traceability, documentation, and preparation of standards.

2.2.1.3 All standards must be identified and quantitated prior to use in the laboratory. This is performed by purchasing certified standard solutions from a commercial supplier that is recognized by the EPA and which are traceable to NIST. In addition, standards for the permanent gases and non-gases are monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if the calibration standard(s) fail to meet the criteria specified in SW 846. Standards for gases need to be replaced after one week, or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards for the non-gases need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. If the standards meet the criteria for the calibration standard(s) as specified in SW 846, they are considered acceptable.

2.2.1.4 All standard solutions are stored in the VOA freezer at -10°C to -20°C. The stock and secondary dilution standards are stored in flame-sealed amber ampules (with the exception of the internal and surrogate standards). The secondary dilution standards are checked for degradation or evaporation prior to preparing calibration standards. Secondary dilution standards should be replaced after one week, unless the acceptability of the standard can be documented. Pre-mixed certified solutions are stored according to the manufacturers' documented holding time and storage temperature recommendations. Prior to daily and initial calibration standard preparation, the standard solutions are removed from the freezer and allowed to warm to room temperature.

2.2.1.5 Refer to Appendix I for a tabular listing of all standard solutions and their concentrations. The additional appendix IX compounds (which are only analyzed upon request) and their standard concentrations are tabulated in Appendix IV.

2.2.2 Preparation of Internal Standards and Surrogate Standards

2.2.2.1 If starting with a neat material, a measured amount of the neat chemical is placed in a glass volumetric and diluted to volume with methanol, then stoppered. 125 mg of neat material is diluted into 25 mL of methanol. This yields an intermediate solution of 5000 µg/mL.

2.2.2.2 Aliquots of the intermediate solutions are taken from the individual internal and surrogate standards and then combined in a volumetric flask and diluted with methanol to yield a working standard which contains all compounds at a concentration of 250 µg/mL each. This is accomplished by using a gas-tight syringe to transfer each aliquot of 1.25 mL into 25 mL of methanol. A 1 µL aliquot of this solution is injected via the autosampler into 5 mL for waters, low and medium level soils (and 25 mL for low level waters) of sample, resulting in an internal and surrogate standard concentration of 50 µg/L (or 10 µg/L for low level waters).

Internal Standards	Surrogate Standards
Fluorobenzene	1,2-Dichloroethane-d4
Chlorobenzene-d5	Toluene-d8
1,4-Dichlorobenzene-d4	p-Bromofluorobenzene
	Dibromofluoromethane

2.2.3 Preparation of Matrix Spike Solution

2.2.3.1 At a minimum five volatile analytes are used for spiking. Upon request by the client additional analytes may be used if they are of interest at the site. A certified matrix spiking solution which contains the five spiking analytes is purchased pre-mixed from a commercial supplier at a concentration of 2500 µg/mL each. This solution is then diluted in methanol to a concentration of 200 µg/mL.

Matrix Spike Solution	Source*	Part Number*
1,1-Dichloroethene	Restek	30005
Benzene		
Trichloroethene		
Toluene		
Chlorobenzene		

* or equivalent

2.2.3.2 A 12.5 µL (2.5 µL for low level waters) aliquot of this solution is spiked into 50 mL of sample, resulting in a spiked concentration of 50 µg/L (or 10 µg/L for low level waters) for each analyte.

Working Concentration	Aliquot	Final Volume	Concentration
Soils, 5 mL Water			
200 µg/mL	12.5 µL	50 mL PFW	50 µg/L
Medium Level Soils			
200 µg/mL	12.5 µL	50 mL PFW	(50 µg/L extract) 5000 µg/L sample
25 mL Water			
200 µg/mL	2.5 µL	50 mL PFW	10 µg/L

2.2.4 Preparation of p-Bromofluorobenzene (BFB) Solution

2.2.4.1 The preparation of BFB is similar to that of the internal standards and surrogate standards. Refer to Section 2.2.2 for details.

2.2.4.2 A solution of 25 ng/L is prepared and stored in flame-sealed amber ampules.

2.2.5 Preparation of Initial Calibration Standards

2.2.5.1 Certified sets of stock solutions which contain all target analytes are purchased pre-mixed from a commercial supplier at a concentration of 2000 µg/mL each. If additional target analytes are requested, these analytes may be ordered separately, either in solution or as a neat material.

2.2.5.2 These solutions are then diluted in methanol to generate standards at concentrations of 200 µg/mL. This solution is stored in flame-sealed amber ampules.

2.2.5.3 Standards are stored in the VOA freezer at -10°C to -20°C. They are removed prior to making up the initial calibration standards and are allowed to warm to room temperature.

2.2.5.4 The initial calibration standards range from 1 µg/L to 50 µg/L for low level waters and 3 µg/L to 200 µg/L for soils, and 5 mL water samples for all target analytes with the exception of the ketones and m,p-xylenes. . Please refer to Appendix I for a tabular

listing of all analytes and calibration concentrations. The 5 mL water calibration standards are also employed in the analysis of medium or high level soils, since the aqueous calibration standards are purged at ambient temperature. Analysis of the solid matrices in the low level format require a purge temperature of 40° C.

2.2.5.5 The standards are prepared by taking aliquots of the solutions and diluting them into a volumetric containing PFW. A 40 mL aliquot is immediately poured into a VOA vial (or a 5 mL aliquot for the low level soils is placed in a soil vessel) and placed on the autosampler. Each standard concentration is prepared just prior to analysis and any remaining standard solution is disposed of once the analytical run is initiated.

Solution	Source*	Part Number*
VOC Mix 1	Supelco	4-8775
VOC Mix 2	Supelco	4-8777
VOC Mix 3	Supelco	4-8779
VOC Mix 4	Supelco	4-8786
VOC Mix 5	Supelco	4-8797
VOC Mix 6	Supelco	4-8799
TCL Mix 1	Supelco	4-8949
Carbon Disulfide	Supelco	4-0363

* or equivalent

Low Level Water (25 mL)

Working Solution	Aliquot non-ketones	Aliquot ketones	Final Volume	Concentrations non-ketones	Concentrations ketones
200 µg/mL	1.0 µL	-	200 mL	1 µg/L	
200 µg/mL	2.5 µL	2.5 µL	100 mL	5 µg/L	5 µg/L
200 µg/mL	5.0 µL	5 µL	100 mL	10 µg/L	10 µg/L
200 µg/mL	12.5 µL	12.5 µL	100 mL	25 µg/L	25 µg/L
200 µg/mL	12.5 µL	12.5 µL	50 mL	50 µg/L	50 µg/L
200 µg/mL	-	25 µL	50 mL	-	100 µg/L

Low Level Soil

Working Solution	Aliquot non-ketones	Aliquot ketones	Final Volume	Concentrations non-ketones	Concentrations ketones
200 µg/mL	1.5 µL	2.5 µL	100 mL/50 mL	3 µg/L	10 µg/L
200 µg/mL	2.5 µL	5 µL	50 mL	10 µg/L	20 µg/L
200 µg/mL	12.5 µL	12.5 µL	50 mL	50 µg/L	50 µg/L
200 µg/mL	5.0 µL	5.0 µL	10 mL	100 µg/L	100 µg/L
200 µg/mL	10.0 µL	10.0 µL	10 mL	200 µg/L	200 µg/L

5 mL Water And Medium Level Soil

Working Solution	Aliquot non-ketones	Aliquot ketones	Final Volume	Concentrations non-ketones	Concentrations ketones
200 µg/mL	1.5 µL	2.5 µL	100 mL/50 mL	3 µg/L	10 µg/L
200 µg/mL	2.5 µL	5 µL	50 mL	10 µg/L	20 µg/L
200 µg/mL	12.5 µL	12.5 µL	50 mL	50 µg/L	50 µg/L
200 µg/mL	25 µL	25 µL	50 mL	100 µg/L	100 µg/L
200 µg/mL	50 µL	50 µL	50 mL	200 µg/L	200 µg/L

2.2.6 Preparation of a Daily Calibration Standard

2.2.6.1 The concentration of the continuing calibration standard at a level of 10 µg/L for low level waters, 50 µg/L for low and medium level soils and 5 mL waters, is also the mid-point of the initial calibration curve. This standard is always prepared just prior to analysis by transferring an aliquot of each of the 200 µg/mL multi-component working solutions into a volumetric containing PFW.

3. Safety precautions & Waste disposal

3.1 Routine Safety Precautions

3.1.1 All standards and samples should be handled as if they are hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.4 Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.5 Flammable solvents such as methanol are stored in the appropriate solvent locker located outside the volatile laboratory.

3.1.6 Many analytes are known or suspected carcinogens. Analysts should take the proper precautions such as wearing gloves when working with suspect samples or high level standards or solvents. Additionally, a respirator should be worn and a fume hood utilized for extremely hazardous compounds.

3.2 Waste disposal

3.2.1 Waste solvents and expired standards are disposed of in the appropriate waste solvent container located in the prep area under the hood.

3.2.2 Solid sample matrices are disposed of in appropriate drums labeled for this specific purpose where they are routinely picked up by an approved agency for final disposal.

4. Operation procedures

4.1 Analytical Conditions

GC Parameters

Injection Port Temperature	: 200°C
GC/MS Interface Temperature	: 250°C
Initial GC Temperature	: 30°C
Initial Hold Time	: 4 min
Ramp Rate	: 4°C/min
Final Temperature	: 140°C
Final Time	: 4 min
Carrier Gas Flow	: 15 mL/min
Column Head Pressure	: 9 psi

Purge and Trap Parameters

Purge Time	: 11 min
Desorb Time	: 1 min
Bake Time	: 16 min
Desorb Preheat Temperature	: 20°C
Desorb Temperature	: 180°C
Purge Flow	: 40 mL/min
Purge Temperature	: Ambient (40°C for soils)
Desorb Flow Rate	: 15 mL/min

Mass Spectrometer Parameters

Electron Energy	: 70 volts
Mass Range	: 35 to 300 amu
Scan Time	: 1.4 sec/scan
Scan Start Time	: 0.1 min

4.2 Method Detection Limit Study

4.2.1 Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in the Laucks SOP for the determination of method detection limits. It involves the analysis of 7 replicate samples spiked at a concentration near the anticipated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL.

4.3 Method Validation

4.3.1 Prior to the analysis of any samples, it is necessary to validate the method. A method validation study is performed in a similar manner to an MDL study with the exception that a minimum of 4 replicates are required and the concentration levels are typically 10-50 times the MDL. In the absence of criteria for the initial demonstration of proficiency, the limits of 70%- 130% can be used.

4.4 Instrument Tuning

4.4.1 Prior to the analysis of any samples, blanks, or calibration standards, the instrument must demonstrate mass calibration and resolution by meeting the established tuning criteria for BFB.

4.4.2 FC-43 (PFTBA) is used as a mass calibrant. The following ratios are suggested in order to meet the tuning criteria for BFB:

Ion	% of ion 69	Isotope	Isotope Abundances
69	100%	70	0.5-1.5%
131	25-40%	132	2.0-4.0%
219	25-40%	220	2.5-5.0%
414	1-3%		

4.4.3 In addition to the tabulated abundances listed above, other criteria should be reviewed at this time.

1) Ion peak widths: The appropriate range is between 0.5 and 0.6 amu. Amu widths beyond this range can lead to loss of minor isotopes, while insufficient peak widths will result in decreased sensitivity.

2) Leak check: The abundances of ions 18, 28, and 32 (water, nitrogen and oxygen, respectively) should be less than 5 percent relative to 69. A level greater than 5 percent is indicative of a leak in the system.

4.4.4 Following the system tuning using FC-43, the GC/MS is then calibrated with BFB. A 2 µL aliquot (1 µL for low level waters) of 25 ng/µL of BFB is injected directly into the GC resulting in a concentration of 50 ng (25 ng for low level waters).

4.4.5 The ion abundances and ratios are checked against the criteria detailed below **or** alternatively, other criteria may be used (e.g., CLP, 524.2). If BFB meets the tuning criteria, then the system is determined to be calibrated. If BFB does not meet the tuning criteria, the GC/MS is re-tuned with FC-43 as described above.

4.4.6 SW 846 allows for the use of 5 - 50 ng of BFB. In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, SW 846 states that the following approach has been shown to be useful: the mass spectrum of BFB may be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not background subtract part of the BFB peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

4.4.7 CLP requires that the three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not background subtract part of the BFB peak.

SW 846 Tuning Criteria

Mass	Abundance %
50	8 - 40% of mass 95
75	30 - 60% of mass 95
95	base peak, 100% relative abundance
96	5 - 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 - 9% of mass 174
176	>95%, < 101% of mass 174
177	5 - 9% of mass 176

CLP Tuning Criteria

Mass	Abundance %
50	8 - 40% of mass 95
75	30 - 66% of mass 95
95	base peak, 100% relative abundance
96	5 - 9% of mass 95
173	< 2% of mass 174
174	50-120% of mass 95
175	4 - 9% of mass 174
176	93 - 101% of mass 174
177	5 - 9% of mass 176

4.5 Initial Multi-Point Calibration

4.5.1 The first option is to begin with the simplest approach, the linear model through the origin using RSDs, as described in section 7.5 of 8000B. In methods where this method is not appropriate, because the calibration acceptance criteria cannot be met, the next option of calibration (linear regression) is used. This calibration option is typically used in fuels because of the elevated response obtained in these analyses. The requirements for the linear regression model is that R^2 be greater than or equal to 0.99. The more complex calibration option is use of the quadratic curve. This calibration option requires a minimum of 6 points and is used in cases where the detector doesn't meet calibration criteria over a wide range. The difficulty with the quadratic is that the intercept may be

greater than the detection limit. This calibration option exhibits a greater accuracy in the mid-range, and may demonstrate more extreme responses at the low and high end of the calibration, and therefore, it is important to dilute samples and extracts so that they are in the mid-range of the calibration.

4.5.2 For linear calibrations using the RSD, analyze standard solutions using a minimum of 5 different concentration levels. The lowest concentration should establish the reporting limit. The highest concentration should define the upper usable working range of the detector. Criteria for evaluating these standards are detailed in Section 6.

4.6 Continuing Calibration Verification

4.6.1 A CCV is analyzed once the BFB tuning criteria have been met and the instrument has been calibrated. Criteria for evaluating a CCV standard are detailed in Section 6.

4.7 Instrument Blank

4.7.1 The analysis of an instrument blank (IBK) is performed prior to the injection of BFB. This analysis ensures that there are no volatile organic contaminants in either the purge and trap sample concentrator or in the autosampler.

4.7.2 Any sample that demonstrates concentrations of target analytes high enough to saturate the detector must be followed by at least one IBLK, also known as a saturation blank. This IBLK analysis is performed to prevent any possible carry-over into the subsequent sample analysis. Evaluation criteria follow the same guidelines set forth for the analysis of a method blank.

4.8 Method Blank

4.8.1 Immediately following the analysis of the CCV and prior to sample analysis, a method blank must be analyzed. The analysis of the method blank demonstrates that the instrument is free of volatile organic contaminants and ensures that the reagent water is also free of contaminants. Refer to Section 6 for method blank acceptance criteria.

4.9 Sample Analysis

4.9.1 Samples (and associated QC) may be analyzed for up to 12 hours from the injection of BFB. The samples are analyzed subsequent to the calibration standard and method blank analyses. However, no more than twenty sample analyses are performed in a 12 hour period. Once all criteria for BFB, the calibration standard, and method blank have been met, the sample analyses are performed. The aqueous and medium level soil samples are

analyzed against an aqueous (non-heated purge) calibration curve. The low level soils are analyzed against a calibration curve employing a heated purge temperature of 40°C.

4.10 Analysis sequence

IBLK (optional)
BFB
CCV
Method blank
Samples and QC

4.11 Sample Preparation

4.11.1 The samples are removed from the VOA refrigerator and are allowed to warm to room temperature. Aqueous samples which are received in 40 mL vials and low level soil samples containing the pre-weighed sample aliquot in sodium bisulfate are placed onto the autosampler carousel. See section 4.11.5 for the preparation of medium soils. The autosampler transfers a 5 mL, or 25 mL aliquot of sample (or an aliquot of PFW for the soils) into the autosampler syringe, where it injects 1 µL of the internal standard and surrogate standard solution.

4.11.2 The pH of all water and low level soil samples is measured subsequent to analysis in order to determine if they were preserved adequately without disturbing the integrity of the sample. The pH values are noted in the instrument logbook.

4.11.3 If the concentration of any target analyte exceeds the initial calibration range, the sample must be diluted and reanalyzed.

4.11.4 If aqueous samples require dilutions, they are diluted by one of two methods listed:

1) the samples are diluted with PFW in a volumetric where they are transferred to 40 mL vials and placed onto the autosampler, or

2) the undiluted samples are placed on the autosampler, where they are diluted with PFW by the autosampler. Refer to the instrumentation manuals for the complete operation of the autosampler.

4.11.5 Medium Soils

4.11.6 The soil sample is gently mixed (no supernatant liquid is removed) and a 5 gram aliquot (weighed out to the nearest 0.1 g) is transferred to a tared 15 mL vial. 10.0 mL of methanol is added to the vial. The vial is sealed, then shaken for two minutes. A 1 mL aliquot is transferred to a GC vial for storage in the dark at 4°C (±2°C). A 100 µL sample aliquot per 5 mL of PFW is placed onto the autosampler carousel. The autosampler transfers a volume of 5 mL of this sample into the autosampler syringe, where it injects 1 µL of the internal standard and surrogate solution.

4.12 Qualitative Identification

4.12.1 Two criteria must be satisfied to verify the identification of target compounds:

1) elution of the sample component within 0.50 minutes of the standard component and,

2) appropriate correspondence between the sample mass spectrum and the standard mass spectrum.

a) The three ions of greatest relative intensity, or any ions over 30% relative intensity which are present in the standard mass spectrum must be present in the sample spectrum.

b) The relative intensities of ions must be within 30% between the standard and sample spectrum.

d) The emphasis of spectral review is on the three major ions. However, if a target compound cannot be verified by all the criteria listed above, but if, in the technical judgment of the analyst, the identification is correct, then the analyte will be quantitated, and reported. Compounds meeting the identification criteria must be reported with their spectra.

4.12.2 A library search may be performed for the purpose of identifying up to 10 largest non-target analytes also referred to as Tentatively Identified Compounds (TICs) if requested by the client. The criteria for confirming TICs are listed below.

1) Relative intensities of ions in the reference spectrum > 10% of the most abundant ion should be present in the sample spectrum.

2) Molecular ions in the reference spectrum should be present in the sample spectrum.

3) The relative intensities for the major ions should agree within 20%.

4) Ions in the sample spectrum but not present in the standard spectrum should be reviewed for possible background contamination or coelution.

4.13 Compound Quantification

4.13.1 Target compound concentrations are calculated using the following equations:

Aqueous samples:

$$\text{Conc } (\mu g / L) = \frac{A_x \times I_s \times Df}{A_{is} \times ARF \times V_o}$$

where:

A_x = Area of the characteristic ion (EICP) of the analyte.
A_{is} = Area of the characteristic ion (EICP) of the internal standard.
I_s = Amount of the internal standard (ng).
ARF = Average RF from the ambient temperature purge of the initial calibration.
V_o = Volume of water purged (mL).
Df = Dilution factor. Assume 1.0 for no dilution.

Low soil (on a dry-weight basis)

$$\text{Conc } (\mu g / kg) = \frac{A_x \times I_s}{A_{is} \times ARF \times W_s \times D}$$

where:

A_x = Area of the characteristic ion (EICP) of the analyte.
A_{is} = Area of the characteristic ion (EICP) of the internal standard.
I_s = Amount of the internal standard (ng).
ARF = Average response factor from the heated purge of the initial calibration.
W_s = Weight of sample added to purge vessel (g).

$$D = \frac{100 - \%\text{Moisture}}{100}$$

Medium soil (on a dry weight basis)

$$\text{Conc } (\mu g / kg) = \frac{A_x \times I_s \times V_t \times 1000 \times Df}{A_{is} \times ARF \times V_a \times W_s \times D}$$

where:

A_x = Area of the characteristic ion (EICP) of the analyte.
A_{is} = Area of the characteristic ion (EICP) of the internal standard.
I_s = Amount of the internal standard (ng).
ARF = Average RF from the ambient temperature purge of the calibration standard.
V_t = Total volume of the methanol extract in milliliters (10 mL).
V_a = Volume of the methanol extract in microliters added to the reagent water for purging.
W_s = Weight of sample added to purge vessel (g).
Df = Dilution factor. Assume 1.0 for no dilution.

5. Reports

5.1 Data Packet Organization

5.1.1 See Appendix II for a check list detailing data packet organization.

5.2 Quality Control Reports

5.2.1 All results for quality control tests are entered into the lab database. Printouts of all data entered must be included in the data packet. The routine minimum is a method blank report, a blank spike report, and a MS/MSD report.

5.3 Control Limits

5.3.1 The laboratory has a computerized database which is used to generate control limits for various analyses, matrices, and analytes. The control limits define the range in which 99% of all values produced by a system should lie. Because the control limits are updated periodically, the current control limits for QC analyses have not been defined in this SOP. A copy of all current control limits are located in Laucks' Control Limits Database.

5.4 Data Qualifying Flags

5.4.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

Code	Definition
U	The analyte of interest was not detected, to the limit of detection indicated.
B	The analyte of interest was detected in the method blank associated with the sample, as well as in the sample itself. The B flag is applied without regard to the relative concentrations detected in the blank and sample.
J	The analyte of interest was detected below the practical quantitation limit. This value should be regarded as an estimate.
D	The value reported is derived from the analysis of a diluted sample or sample extract.
E	The value reported is based on a sample or sample extract in which the target analyte concentration exceeded the calibration range. The value reported should be considered an estimate.
N	Used to denoted the presumptive evidence of a target analyte. This flag is used when it is not possible to confirm the presence of a compound by the strict guidelines for mass spectral interpretation, but in the technical judgment of the analyst, this compound is present.

6. Quality Control

6.1 Initial Calibration

6.1.1 Criteria

6.1.1.1 Initial calibration data are evaluated using %RSD and the relative response factors.

RFs are calculated using the equation:

$$RF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_s}$$

where:

A_x = Response of target analyte
A_{is} = Response of internal standard
C_x = Amount of target analyte (ng/mL).
C_{is} = Amount of internal standard (ng/mL).

%RSDs are calculated using the equation:

$$\%RSD = \frac{SD_i}{RF_i} \times 100$$

where:

Sd_i = Standard deviation of the initial calibration points
RF_i = Average RF from initial calibration

6.1.2 The System Performance Check Compounds (SPCCs) are checked to determine that the minimum average relative response factors tabulated below are met, and that the maximum RSD for each Calibration Check Compound (CCC) is < 30%. The RSD for all other target analytes *should* be ≤ 15%. If the RSD of any target analyte is greater than 15%, but < 30%, additional calibration options may be used. Alternatively, if the mean of the RSD values for all analytes in the calibration is < 15%, the initial calibration is considered acceptable. Laucks uses 40% percent as the upper limit for all compounds as an internal guideline although it is not a requirement of SW 846.

6.1.2.1 The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project.

6.1.2.2 The data used must be supplied with either a summary of the initial calibration data or a specific list of those compounds for which the RSD exceeded 15% and the results of the mean RSD calculation.

SPCC Compounds	Minimum RF Limit
Chloromethane	0.100
1,1-Dichloroethane	0.100
Bromoform	0.100
Chlorobenzene	0.300
1,1,2,2-Tetrachloroethane	0.300

CCC Compounds	%RSD Limit
Vinyl chloride	<30%
1,1-Dichloroethene	<30%
Chloroform	<30%
1,2-Dichloropropane	<30%
Toluene	<30%
Ethylbenzene	<30%

6.1.2.3 For Navy samples, an additional criterion of a minimum RRF of 0.005 for all other reported analytes (with the exception 25 mL purges) has been implemented.

6.1.3 Corrective action

6.1.3.1 If the criteria are not met, additional standards may be analyzed or appropriate instrument maintenance and analysis of new standards should be performed.

6.1.4 Documentation

6.1.4.1 Copies of the initial calibration standards and the calculated RRFs and RSDs are stored with the raw data. If criteria are not met, reanalysis of additional standard(s) are noted in the instrument run log.

6.2 Continuing Calibration Verification

6.2.1 Criteria

6.2.1.1 At the beginning of each 12 hour QC period, a CCV standard is analyzed. The RRF for each compound is calculated and the percent difference is calculated as follows:

$$\%D = \frac{RF_i - RF_c}{RF_i} \times 100$$

where:

RF_i = Average RF from Initial Calibration
RF_c = RF from CCV standard

6.2.1.2 The minimum RRFs for the SPCCs must meet the criteria applied in the initial calibration detailed above. The %D for the CCCs cannot exceed the 20% CCV criteria as tabulated below.

CCC Compounds	% D Limit
1,1-Dichloroethene	<20%
Chloroform	<20%
1,2-Dichloropropane	<20%
Toluene	<20%
Ethylbenzene	<20%
Vinyl chloride	<20%

6.2.1.3 Laucks uses a maximum %D of 40% for all other reported analytes as an internal guideline, although it is not a requirement of SW 846.

6.2.2 Corrective action

6.2.2.1 Check calculations, check standard solutions or perform instrument maintenance. Reanalyze the standard, if this fails, re-do initial calibration.

6.2.3 Documentation

6.2.3.1 Copies of the continuing calibration standards and the calculated RFs and %Ds are stored with the raw data. If criteria are not met, reanalysis of additional standard(s) are noted in the instrument run log.

6.3 Instrument Blank

6.3.1 Criteria

6.3.1.1 The criteria used are the same as those used for the method blank control limits.

6.3.2 Corrective action

6.3.2.1 If the initial IBLK contains measurable levels of target analytes above one-half the reporting limit, except where noted below, the system is out of control. The source of contamination must be identified and corrected. If analysis of an additional IBLK does not demonstrate that the analytical system if free of contaminants, then instrument maintenance such as cleaning the transfer lines or replacing the trap may be required.

6.3.3 Documentation

6.3.3.1 Copies of instrument blank analyses are stored with the sample analyses raw data. Re-analysis of the method blank and/or maintenance performed is documented in the instrument run log.

6.4 Method Blanks

6.4.1 Criteria

6.4.1.1 A method blank is used to verify contamination free reagents and apparatus. A method blank is analyzed following every CCV and prior to sample analysis. The results of the method blank should be:

6.4.1.2 Laucks criteria for a method blank is less than one-half the RL for each analyte, or less than 5 percent of the regulatory limit associated with that analyte, or less than 5 percent of the sample result for the same analyte, whichever is greater for the method blank to be acceptable.

6.4.2 Corrective action

6.4.2.1 When this criteria is exceeded, corrective action should be taken to find/reduce/eliminate the source of this contamination in the method blank. Sample corrective action may be limited to qualification for blank contamination. When the concentrations of any target analytes within the method blank are above one-half of the reporting limit for the majority of target analytes or above the reporting limit for target

analytes known to be common laboratory contaminants, the effect this may have had on the samples will be assessed. If any analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps shall be taken to find/reduce/eliminate ths source of this contamination in the method blank. The case narrative should also discuss the situation. If an analyte is found in the method blank and some, or all, of the other batch samples, additional corrective action is required to reanalyze the method blank, and any samples containing the same contaminant. If the contamination remains, the contaminated samples of the batch would be reprepared and reanalyzed with a new method and batch specific QC samples. Sporadic cases of contamination may be difficult to control, however, daily contamination would not be acceptable.Out-of-control surrogate recoveries in the method blank require reanalysis of the method blank.

6.4.3 Documentation

6.4.3.1 Copies of all method blank analyses are stored with the sample analyses raw data. In addition, the raw data for the method blank analyses are stored in the laboratory for an extended period of time. The results for the method blank analyses are reported electronically via the laboratory's LIMS database. If criteria are not met, reanalysis of additional blank(s) are noted in the instrument run log. Outliers are discussed in the case narrative.

6.5 Blank Spikes

6.5.1 Criteria

6.5.1.1 A blank spike follows the same protocol as a matrix spike analysis except that the spiking solution is added to an aliquot of PFW (or sand for soil samples) instead of an actual sample. A method blank with added analytes is a blank spike. A blank spike is the same as a QC check standard. It is recommended that all target analytes of concern be spiked into the LCS. A subset of the single-component target analytes can be substituted for the full list if specified in project-specific contracts or workplans per the USACOE Shell document.

6.5.2 Corrective action

6.5.2.1 The blank spike is used to determine whether a method is in control during sample preparation and analysis. Sample reanalysis would be triggered by an out of control blank spike only if the sample surrogate recoveries and MS/MSD spike recoveries indicated sample processing errors.

6.5.3 Documentation

6.5.3.1 The raw data for the blank spike analyses are stored in the laboratory for an extended period of time. The results for the blank spike analyses are reported electronically via the laboratory's LIMS database. If criteria are not met, reanalysis of additional blank spike(s) are noted in the instrument run log.

6.6 Matrix Spike

6.6.1 Criteria

6.6.1.1 A sample is chosen at random (unless specified by a client) from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to analysis. A matrix spike analysis is performed with each analytical batch, up to a maximum of 20 samples. The matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$\text{Recovery} = \frac{SS - S}{SpikedAmount} \times 100$$

where:

SS = concentration in spiked sample
S = native concentration in unspiked sample

6.6.2 Corrective action

6.6.2.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action may involve recalculation and/or reanalysis. This process should also include evaluation of the recovery of surrogate compounds in the MS sample and recovery of matrix spiking compounds from the blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

6.6.3 Documentation

6.6.3.1 The raw data for the matrix spike analyses are stored with the sample analyses raw data. The results for the matrix spike analyses are reported electronically via the laboratory's LIMS database.

6.7 Matrix Spike Duplicate

6.7.1 Criteria

6.7.1.1 A matrix spike duplicate analysis is performed with each analytical batch, up to a maximum of 20 samples. The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used to measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values. This calculation is as follows:

$$RPD = \frac{S1 - S2}{(S1 + S2) \backslash 2} \times 100$$

where:

S1 = measured concentration for MS sample
S2 = measured concentration for MSD sample

6.7.2 Corrective action

6.7.2.1 If a trend in out-of-control RPD values is observed, the method used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility.

6.7.3 Documentation

6.7.3.1 The raw data for the matrix spike duplicate analyses are stored with the sample analyses raw data. The results for the matrix spike duplicate analyses are reported electronically via the laboratory's LIMS database. Any out-of-control results are documented in the LIMS database and/or analytical narrative.

6.8 Surrogate Recovery

6.8.1 Criteria

6.8.1.1 Surrogates are chemically similar compounds added to every sample, method blank, and QC sample prior to sample processing. They are used to monitor potential sample processing errors and matrix effects. Surrogate compound recoveries are calculated as follow:

$$\text{Recovery} = \frac{S_m}{S_a} \times 100$$

where:

S_m = concentration of surrogate measured in sample
S_a = concentration of surrogate added

6.8.2 Corrective Action

6.8.2.1 Check calculations for possible error. Reanalysis is required for all surrogate recoveries which exceed the established control limits.

6.8.2.2 Out-of-control surrogate recoveries in the method blank require that the method blank be reanalyzed. Sample analyses are not performed until all criteria are met in the method blank analysis. Sample and QC analyses require reanalysis for out-of-control surrogate recoveries. If the sample reanalyses also demonstrate out-of-control surrogate recoveries due to matrix interference, this corrective action is discussed in the narrative.

6.8.3 Documentation

6.8.3.1 The surrogate recoveries for all samples, blanks, and QC analyses are reported electronically via the laboratory's LIMS database. If criteria are not met, reanalysis of for out-of-control surrogate recoveries are designated by an "RE" in the instrument run log.

7. References

1) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, (SW-846), US EPA Office of Solid Waste and Emergency Response, - Method 8260B, 3rd edition, 2nd revision, December 1996.

2) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, (SW-846), US EPA Office of Solid Waste and Emergency Response, - Method 8000B, 3rd edition, 2nd revision, December 1996.

3) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, (SW-846), US EPA Office of Solid Waste and Emergency Response, - Method 5000B, 3rd edition, revision 0, December 1996.

4) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, (SW-846), US EPA Office of Solid Waste and Emergency Response, - Method 5030B, 3rd edition. 2nd revision, December 1996.

5) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, (SW-846), US EPA Office of Solid Waste and Emergency Response, - Method 5035, 3rd edition, revision 0, December 1996.

APPENDIX I

Initial Calibration Concentrations For Low Level (25 mL) Waters (µg/L)

Compound	STD1	STD2	STD3	STD4	STD5
Dichlorodifluoromethane	1	5	10	25	50
Chloromethane	1	5	10	25	50
Vinyl Chloride	1	5	10	25	50
Bromomethane	1	5	10	25	50
Chloroethane	1	5	10	25	50
Trichlorofluoromethane	1	5	10	25	50
1,1-Dichloroethene	1	5	10	25	50
Acetone	5	10	20	50	100
Carbon disulfide	1	5	10	25	50
Methylene chloride	1	5	10	25	50
trans-1,2-Dichloroethene	1	5	10	25	50
1,1-Dichloroethane	1	5	10	25	50
Vinyl acetate	1	5	10	25	50
2,2-Dichloropropane	1	5	10	25	50
cis-1,2-Dichloroethene	1	5	10	25	50
2-Butanone	5	10	20	50	100
Bromochloromethane	1	5	10	25	50
Chloroform	1	5	10	25	50
1,1,1-Trichloroethane	1	5	10	25	50
Carbon tetrachloride	1	5	10	25	50
1,1-Dichloropropene	1	5	10	25	50
Benzene	1	5	10	25	50
1,2-Dichloroethane	1	5	10	25	50
Trichloroethene	1	5	10	25	50
1,2-Dichloropropane	1	5	10	25	50
Dibromomethane	1	5	10	25	50
Bromodichloromethane	1	5	10	25	50
cis-1,3-Dichloropropene	1	5	10	25	50
4-Methyl-2-pentanone	5	10	20	50	100
Toluene	1	5	10	25	50
trans-1,3-Dichloropropene	1	5	10	25	50

Compound	STD1	STD2	STD3	STD4	STD5
1,1,2-Trichloroethane	1	5	10	25	50
Tetrachloroethene	1	5	10	25	50
1,3-Dichloropropane	1	5	10	25	50
2-Hexanone	5	10	20	50	100
Chlorodibromomethane	1	5	10	25	50
1,2-Dibromoethane	1	5	10	25	50
Chlorobenzene	1	5	10	25	50
1,1,1,2-Tetrachloroethane	1	5	10	25	50
Ethylbenzene	1	5	10	25	50
m,p-Xylene	2	10	20	50	100
o-Xylene	1	5	10	25	50
Styrene	1	5	10	25	50
Bromoform	1	5	10	25	50
Isopropylbenzene	1	5	10	25	50
Bromobenzene	1	5	10	25	50
1,2,3-Trichloropropane	1	5	10	25	50
1,1,2,2-Tetrachloroethane	1	5	10	25	50
n-Propylbenzene	1	5	10	25	50
2-Chlorotoluene	1	5	10	25	50
4-Chlorotoluene	1	5	10	25	50
1,3,5-Trimethylbenzene	1	5	10	25	50
tert-Butylbenzene	1	5	10	25	50
1,2,4-Trimethylbenzene	1	5	10	25	50
sec-Butylbenzene	1	5	10	25	50
1,3-Dichlorobenzene	1	5	10	25	50
1,4-Dichlorobenzene	1	5	10	25	50
p-Isopropyltoluene	1	5	10	25	50
1,2-Dichlorobenzene	1	5	10	25	50
n-Butylbenzene	1	5	10	25	50
1,2-Dibromo-3-chloropropane	1	5	10	25	50
1,2,4-Trichlorobenzene	1	5	10	25	50
Naphthalene	1	5	10	25	50
Hexachlorobutadiene	1	5	10	25	50
1,2,3-Trichlorobenzene	1	5	10	25	50

Initial Calibration Concentrations Of Routine Target Analytes For Low And Medium Level Soils & 5 mL Waters

Compound (µg/L)	STD1	STD2	STD3	STD4	STD5
Dichlorodifluoromethane	3	10	50	100	200
Chloromethane	3	10	50	100	200
Vinyl Chloride	3	10	50	100	200
Bromomethane	3	10	50	100	200
Chloroethane	3	10	50	100	200
Trichlorofluoromethane	3	10	50	100	200
1,1-Dichloroethene	3	10	50	100	200
Acetone	10	20	50	100	200
Carbon disulfide	3	10	50	100	200
Methylene chloride	3	10	50	100	200
trans-1,2-Dichloroethene	3	10	50	100	200
1,1-Dichloroethane	3	10	50	100	200
cis-1,2-Dichloroethene	3	10	50	100	200
2-Butanone	10	20	50	100	200
Chloroform	3	10	50	100	200
1,1,1-Trichloroethane	3	10	50	100	200
Carbon tetrachloride	3	10	50	100	200
Benzene	3	10	50	100	200
1,2-Dichloroethane	3	10	50	100	200
Trichloroethene	3	10	50	100	200
1,2-Dichloropropane	3	10	50	100	200
Bromodichloromethane	3	10	50	100	200
cis-1,3-Dichloropropene	3	10	50	100	200
4-Methyl-2-pentanone	10	20	50	100	200
Toluene	3	10	50	100	200
trans-1,3-Dichloropropene	3	10	50	100	200
1,1,2-Trichloroethane	3	10	50	100	200
Tetrachloroethene	3	10	50	100	200
2-Hexanone	10	20	50	100	200
Chlorodibromomethane	3	10	50	100	200
Chlorobenzene	3	10	50	100	200
Ethylbenzene	3	10	50	100	200
m,p-Xylene	6	20	100	200	400
o-Xylene	3	10	50	100	200
Styrene	3	10	50	100	200

Compound (µg/L)	STD1	STD2	STD3	STD4	STD5
Bromoform	3	10	50	100	200
1,1,2,2-Tetrachloroethane	3	10	50	100	200

Initial Calibration Concentrations Of
Additional Analytes For Low And Medium Level Soils & 5 mL Waters

Compound (µg/L)	STD1	STD2	STD3	STD4	STD5
1,1,1,2-Tetrachloroethane	3	10	50	100	200
2,2-Dichloropropane	3	10	50	100	200
Bromochloromethane	3	10	50	100	200
1,1-Dichloropropene	3	10	50	100	200
1,2-Dibromoethane	3	10	50	100	200
Dibromomethane	3	10	50	100	200
1,3-Dichloropropane	3	10	50	100	200
Isopropylbenzene	3	10	50	100	200
Bromobenzene	3	10	50	100	200
1,2,3-Trichloropropane	3	10	50	100	200
n-Propylbenzene	3	10	50	100	200
2-Chlorotoluene	3	10	50	100	200
4-Chlorotoluene	3	10	50	100	200
1,3,5-Trimethylbenzene	3	10	50	100	200
tert-Butylbenzene	3	10	50	100	200
1,2,4-Trimethylbenzene	3	10	50	100	200
sec-Butylbenzene	3	10	50	100	200
1,3-Dichlorobenzene	3	10	50	100	200
1,4-Dichlorobenzene	3	10	50	100	200
p-Isopropyltoluene	3	10	50	100	200
1,2-Dichlorobenzene	3	10	50	100	200
n-Butylbenzene	3	10	50	100	200
1,2-Dibromo-3-chloropropane	3	10	50	100	200
1,2,4-Trichlorobenzene	3	10	50	100	200
Naphthalene	3	10	50	100	200
Hexachlorobutadiene	3	10	50	100	200
1,2,3-Trichlorobenzene	3	10	50	100	200
Iodomethane	3	10	50	100	200
trans-1,4-Dichloro-2-butene	3	10	50	100	200

APPENDIX II

Data Packet Sequence

1. QC Summary
   - Surrogate recoveries
   - MS/MSD summary
   - Method blank summary
   - Instrument performance check (tuning)
   - Internal standard areas and RT summary

2. Sample Data
   - Target compound results
   - TICs (if requested)
   - Chromatogram normalized to nonsolvent peak
   - Quantitation report
   - Spectra

3. Standards Data
   - Initial calibration form
   - Chromatograms
   - Quantitation reports

   - CCV form
   - Chromatograms
   - Quantitation reports

4. Raw QC
   - BFB tune spectrum, chromatogram, and tabular listing
   - Method blank results, TICs, chromatogram, quantitation report, and spectra
   - MS/MSD results, chromatogram, quantitation report, spectra and control charts

5. Bench Sheets
   - Copy of instrument logbook, copy of COC, copy of holding blank analysis

6. Narrative.

7. Electronic Disk Deliverables (EDD) when requested

8. Control charts

APPENDIX III

Determination of Vinyl Chloride by Selected Ion Monitoring (SIM)

Analytical Conditions:

GC Parameters

Injection Port Temperature	: 200°C
GC/MS Interface Temperature	: 250°C
Initial GC Temperature	: 30°C
Initial Hold Time	: 0 min
Ramp Rate	: 6°C/min
Final Temperature	: 105°C
Final Time	: 0 min
Carrier Gas Flow	: 15 mL/min
Column Head Pressure	: 9 psi

Purge and Trap Parameters

Purge Time	: 11 min
Desorb Time	: 1 min
Bake Time	: 16 min
Desorb Preheat Temperature	: 20°C
Desorb Temperature	: 180°C
Purge Flow	: 40 mL/min
Purge Temperature	: Ambient
Desorb Flow Rate	: 15 mL/min

Mass Spectrometer Parameters

Electron Energy	: 70 volts
Acquisition Start Time	: 0.1 min

Group 1:

M/Z	Dwell Time (milliseconds)
61	50
62	400
63	50
64	50

Group 2:

M/Z	Dwell Time (milliseconds)
49	50
51	50
128	100
129	50

Group 3:

M/Z	Dwell Time (milliseconds)
65	50
67	50
102	50
104	50

Standards:

Internal Standard: Bromochloromethane
Surrogate: 1,2-Dichloroethane-d4

APPENDIX IV

Additional Appendix IX Compounds And Their Initial Concentrations For Low Level (25mL) Waters

Compound* (µg/L)	STD1	STD2	STD3	STD4	STD5
Acrolein	10	20	50	100	200
Bromoethane	10	20	50	100	200
Allyl chloride	10	20	50	100	200
Acrylonitrile	10	20	50	100	200
Chloroprene	10	20	50	100	200
Methacrylonitrile	10	20	50	100	200
Ethyl methacrylate	10	20	50	100	200
Methyl methacrylate	10	20	50	100	200
trans-1,4-Dichloro-2-butene	10	20	50	100	200
2-Chloroethylvinyl ether[1]	10	20	50	100	200

* The calibration range defines the reporting range for these compounds. However, the reporting limits may change for individual projects, based on MDLs, mass spectral confirmation, or project-specific requirements.

1 This analyte is not recommended because it decomposes in water, and does not recover in acidified samples.

APPENDIX V

Method 8260 Requirements and Corrective Actions

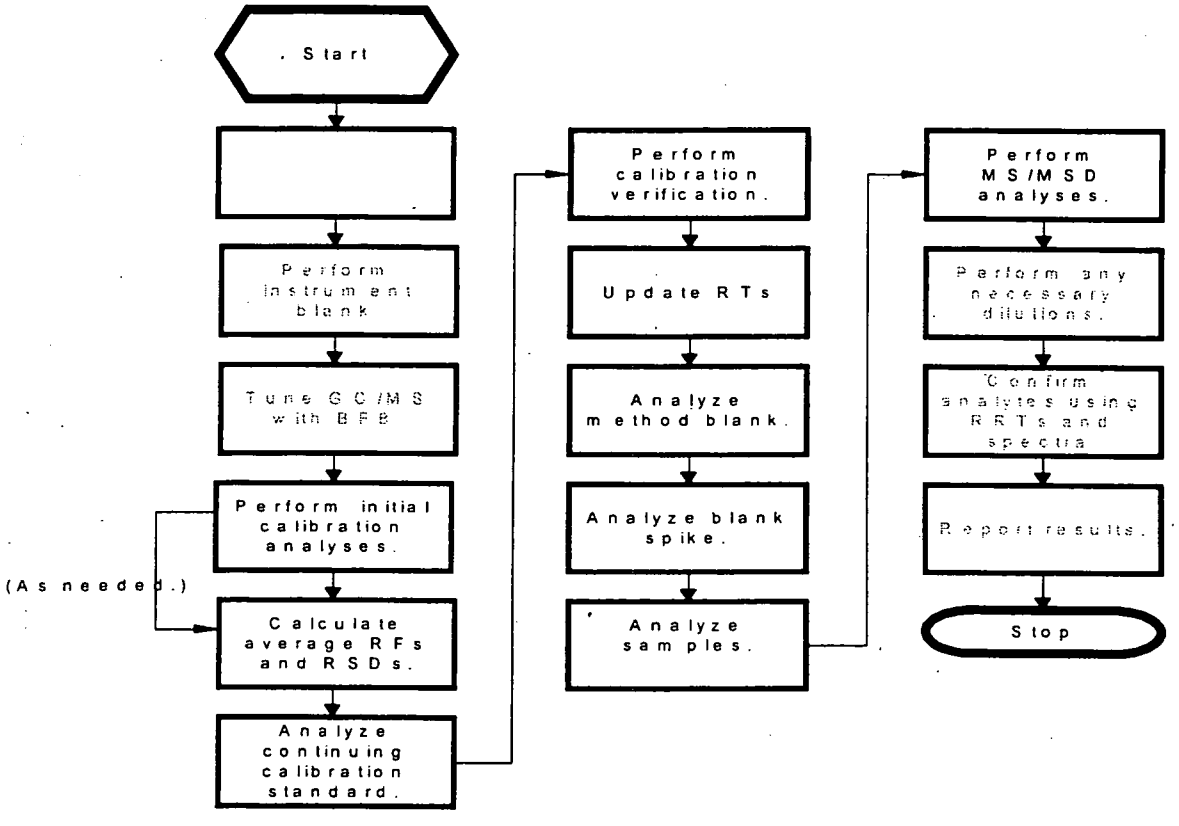
QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Holding Time	14 days from collection.	14 days from collection.	N/A	N/A	HTVR (holding time violation report).
Tuning Verification 5 - 50 ng BFB	Mass Abundance 50 15-40% of 95 75 30-60% of 95 95 100% 96 5-9% of 95 173 < 2% of 174 174 > 50% of 95 175 5-9% of 174 176 95-101% of 174 177 5-9% of 176 *Alternate tuning criteria may be used (e.g.,CLP,524.2).	Mass Abundance 50 8-40% of 95 75 30-66% of 95 95 100% 96 5-9% of 95 173 < 2% of 174 174 50-120% of 95 175 4-9% of 174 176 93-101% of 174 177 5-9% of 176 * Alternate tuning criteria may be used.	Every 12 hours.	Re-tune instrument to meet criteria.	Copy of BFB raw data and tune criteria with file.
Initial Calibration Verification	Minimum of 5 levels with lowest near RL. %RSD for CCCs < 30%. RF for SPCCs: chloromethane 0.10 1,1-dichloroethane 0.10 bromoform 0.10 chlorobenzene 0.30 1,1,2,2-tetrachloroethane 0.30 Non-CCCs: all analytes or average of all analytes = ≤15%.	5 levels 1, 5, 10, 20, 50 µg/L. (Ketones 5,10,20,50,100 µg/L) %RSD for CCCs < 30 %. RFs for SPCCs: chloromethane 0.10 1,1-dichloroethane 0.10 bromoform 0.10 chlorobenzene 0.30 1,1,2,2-tetrachloroethane 0.30 Non-CCCs: all analytes or average of all analytes ≤15%. 40%RSD for each analyte as guideline.	Initially.	Reanalysis of out of control standards.	Copies of all raw data, tune file, and Form VI.
Continuing Calibration Verification	Mid-level calibration standard every 12 hours. RF for SPCCs same as initial. RF for CCCs must be < 20% D.	%D for CCC < 20%, %D for all other compounds < 40% as laboratory guideline.	Every 12 hours.	Reanalyze for analytes that exceed the control limits.	Copies of raw data and Form VII.
Internal Standards	Fluorobenzene, chlorobenzene-d5, 1,4-dichlorobenzene-d4, recommended.	Fluorobenzene, chlorobenzene-d5 and 1,4-dichlorobenzene-d4. RT must be ± 30 seconds from last calibration; area must be 50 to 100%.	Every sample.	Reanalyze all samples that do not meet these criteria.	IS areas and RTs are submitted on Form 8, and included in data package.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Method Blank/ Instrument Blank	One method blank per extraction batch (up to 20 samples) or when there is a change in reagents, whichever is more frequent.	< 1/2 Reporting limit for all analytes, except for methylene chloride, acetone < reporting limit.	One method blank per QC period, following the CCV, prior to sample analysis. Typically, an instrument blank is analyzed prior to tuning the instrument.	Evaluate, qualify.	Copies of raw data filed, and reported electronically. Daily control charts for all method blanks are recorded.
Surrogate Standards	4-bromofluorobenzene, dibromofluoromethane 1,2-dichloroethane-d4 or toluene-d8 recommended. Compare %R to laboratory established limits.	1,2-dichloroethane-d4, toluene-d8, 4-bromofluorobenzene, and dibromofluoromethane. Percent recoveries must meet established laboratory control limits. See QC database for control limits.	Every sample.	Reanalysis if surrogate recoveries exceed the established control limits.	Surrogates that exceed the control limits are documented in associated file.
Quality Control	One MS/MSD per 20 samples or each batch of samples, whichever is more frequent. Compare % recovery to laboratory established limits.	Blank spike recoveries and RPDs must meet control limits established by laboratory. MS/MSD recoveries are allowed to be out if due to matrix effect. See QC database for control limits.	One MS/MSD per 20 samples. A blank spike is analyzed every QC period.	Reanalysis of MS/MSD unless matrix effect has already been demonstrated. This can be determined by comparing with the blank spike recoveries.	Blank spike and MS/MSD recoveries are stored electronically. Raw data is stored with file. Out of control eve are notated in file.
Qualitative Identification	All ions > 10% intensity must be ± 20% of standard; ± 0.06 RRT units of standard RRT.	All ions > 10% intensity must be ± 20% of standard; ± 0.50 min. of standard RT.	For identifying all target analytes in each sample.		Copies of all mass spectra stored with data.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Sample Preservation and Storage	pH ≤2 with HCL for waters. pH ≤ 2 with sodium bisulfate for low level soils. Medium soils: zero headspace, methanol, or EnCore™ sampler. Store at 4 ° C.	pH ≤2 with HCL for waters. pH ≤2 with sodium bisulfate for low level soils. Medium soils: zero headspace, methanol, or EnCore™ sampler. Store at 4° C.	All water and low level soil samples.	If the water and low level soil samples are not acid-preserved, this is narrated in final report.	pH of all water samples and low level soils, where not preserved to a pH of ≤2, noted in instrument logbook.
Standard Solution Expiration	Stock standards (except gases): 6 months. Store between -10 to -20° C in teflon-sealed liners and amber bottles with minimal headspace, protect from light. Stock gas standards: 2 months. Storage conditions same as stock standards. Calibration standards: daily.	Stock standards (except gases): 6 months. Gas stock standards: 2 months. Stored at -10° to -20° C . Calibration standards: daily. All standards sealed in flame-sealed ampules: 2 years (not to exceed parent expiration date).			All standard data recorded in standard logbook.
Field Sample Amount	2 40 mL vials with zero headspace. Soils: vials, with zero headspace, or a sample aliquot in 40 mL vial. Glass container, septum-sealed screw-caps.	Waters:4 40 mL vials with zero headspace. Soils: 2 oz vials, with zero headspace, or a sample aliquot in 4 -40 mL vial. Glass container, septum-sealed screw-caps.			Bottles received by laboratory documented electronically.
Applicability	Groundwaters, soils, sediments, sludges, non-water miscible wastes and others.				

APPENDIX VI

Method 8260B Flow Chart



Refer to corrective action chart for out of control events.

APPENDIX VII

Method 8260 Target Analytes

Dichlorodifluoromethane	Chloromethane
Vinyl Chloride	Bromomethane
Chloroethane	Trichlorofluoromethane
1,1-Dichloroethene	Acetone
Carbon disulfide	Methylene chloride
trans-1,2-Dichloroethene	1,1-Dichloroethane
1,1,2,2-Tetrachloroethane	2,2-Dichloropropane
cis-1,2-Dichloroethene	2-Butanone
Bromochloromethane	Chloroform
1,1,1-Trichloroethane	Carbon tetrachloride
1,1-Dichloropropene	Benzene
1,2-Dichloroethane	Trichloroethene
1,2-Dichloropropane	Dibromomethane
Bromodichloromethane	cis-1,3-Dichloropropene
4-Methyl-2-pentanone	Toluene
trans-1,3-Dichloropropene	1,1,2-Trichloroethane
Tetrachloroethene	1,3-Dichloropropane
2-Hexanone	Chlorodibromomethane
1,2-Dibromoethane	Chlorobenzene
1,1,1,2-Tetrachloroethane	Ethylbenzene
m,p-Xylene	o-Xylene
Styrene	Bromoform

APPENDIX VIII

Method 8260 Optional Analytes for Low Level (25 mL) Water Analyses

Isopropylbenzene	Bromobenzene
1,2,3-Trichloropropane	2-Chlorotoluene
n-Propylbenzene	1,3,5-Trimethylbenzene
4-Chlorotoluene	1,2,4-Trimethylbenzene
tert-Butylbenzene	1,3-Dichlorobenzene
sec-Butylbenzene	p-Isopropyltoluene

Method 8260 Optional Analytes for Low Level (25 mL) Water Analyses

1,4-Dichlorobenzene	n-Butylbenzene
1,2-Dichlorobenzene	1,2,4-Trichlorobenzene
1,2-Dibromo-3-chloropropane	Hexachlorobutadiene
Naphthalene	1,2,3-Trichlorobenzene
Vinyl acetate	

Appendix IX

Additional Appendix IX Compounds (25 mL)

Acrolein	Bromoethane
Allyl chloride	Acrylonitrile
Chloroprene	Methacrylonitrile
Methyl methacrylate	trans-1,4-Dichloro-2-butene
2-Chloroethylvinyl ether	Ethyl methacrylate
Iodomethane	

APPENDIX X

Target Analytes And Their Associated Internal Standards

Fluorobenzene	**Chlorobenzene-d5**	**1,4-Dichlorobenzene-d4**
Dichlorodifluoromethane	Toluene	Isopropylbenzene
Chloromethane	trans-1,3-Dichloropropene	Bromobenzene
Vinyl Chloride	1,1,2-Trichloroethane	1,2,3-Trichloropropane
Bromomethane	Tetrachloroethene	1,1,2,2-Tetrachloroethane
Chloroethane	1,3-Dichloropropane	n-Propylbenzene
Trichlorofluoromethane	2-Hexanone	2-Chlorotoluene
1,1-Dichloroethene	Chlorodibromomethane	4-Chlorotoluene
Acetone	1,2-Dibromoethane	1,3,5-Trimethylbenzene
Carbon disulfide	Chlorobenzene	tert-Butylbenzene
Methylene chloride	1,1,1,2-Tetrachloroethane	1,2,4-Trimethylbenzene
trans-1,2-Dichloroethene	Ethylbenzene	sec-Butylbenzene
1,1-Dichloroethane	m,p-Xylene	1,3-Dichlorobenzene
Vinyl acetate	o-Xylene	1,4-Dichlorobenzene

Fluorobenzene	**Chlorobenzene-d5**	**1,4-Dichlorobenzene-d4**
2,2-Dichloropropane	Styrene	p-Isopropyltoluene
cis-1,2-Dichloroethene	Bromoform	1,2-Dichlorobenzene
2-Butanone		n-Butylbenzene
Bromochloromethane		1,2-Dibromo-3-chloropropane
Chloroform		1,2,4-Trichlorobenzene
1,1,1-Trichloroethane		Naphthalene
Carbon tetrachloride		Hexachlorobutadiene
1,1-Dichloropropene		1,2,3-Trichlorobenzene
Benzene		
1,2-Dichloroethane		
Trichloroethene		
1,2-Dichloropropane		
Dibromomethane		
Bromodichloromethane		
cis-1,3-Dichloropropene		
4-Methyl-2-pentanone		

Additional Appendix IX Compounds And Associated Internal Standard

Fluorobenzene (IS)	**Chlorobenzene-d5**
Acrolein	Ethyl methacrylate
Bromoethane	
Allyl chloride	
Acrylonitrile	
Chloroprene	
Methacrylonitrile	
Methyl methacrylate	
trans-1,4-Dichloro-2-butene	
Iodomethane	
2-Chloroethylvinyl ether	

APPENDIX XI

Target Analytes And Their Quantitation Ions

Compound	Primary Quant Ions*	Secondary Quant Ions*
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl Chloride	62	64
Bromomethane	96	94
Chloroethane	64	66
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61,63
Acetone	43	58
Carbon disulfide	76	78
Methylene chloride	84	86
trans-1,2-Dichloroethene	96	98,61
1,1-Dichloroethane	63	65,83
2,2-Dichloropropane	77	97
cis-1,2-Dichloroethene	96	98,61
2-Butanone	43	57
Bromochloromethane	128	49,130
Chloroform	83	85
1,1,1-Trichloroethane	97	99,61
Carbon tetrachloride	117	119
1,1-Dichloropropene	75	77,110
Benzene	78	-
1,2-Dichloroethane	62	98
Trichloroethene	95	97,130,132
1,2-Dichloropropane	63	112
Dibromomethane	93	95,174
Bromodichloromethane	83	85,127
cis-1,3-Dichloropropene	75	77
4-Methyl-2-pentanone	43	58,85
Toluene	92	91

Compound	Primary Quant Ions*	Secondary Quant Ions*
trans-1,3-Dichloropropene	75	77
1,1,2-Trichloroethane	83	97,85
Tetrachloroethene	166	164
1,3-Dichloropropane	76	78
2-Hexanone	43	58,100
Chlorodibromomethane	129	208,206
1,2-Dibromoethane	107	109
Chlorobenzene	112	114
1,1,1,2-Tetrachloroethane	131	133
Ethylbenzene	91	106
m,p-Xylene	106	91
o-Xylene	106	91
Styrene	104	78
Bromoform	173	175
Isopropylbenzene	105	120
Bromobenzene	156	158
1,2,3-Trichloropropane	75	77
1,1,2,2-Tetrachloroethane	83	85
n-Propylbenzene	120	91
2-Chlorotoluene	126	91
4-Chlorotoluene	91	126
1,3,5-Trimethylbenzene	105	120
tert-Butylbenzene	91	134,119
1,2,4-Trimethylbenzene	105	120
sec-Butylbenzene	105	134

Compound	Primary Quant Ions*	Secondary Quant Ions*
1,3-Dichlorobenzene	146	148,111
1,4-Dichlorobenzene	146	148,111
p-Isopropyltoluene	119	134,91
1,2-Dichlorobenzene	146	148,111
n-Butylbenzene	91	92
1,2-Dibromo-3-chloropropane	75	155,157
1,2,4-Trichlorobenzene	180	182
Naphthalene	128	-
Hexachlorobutadiene	225	223,227
1,2,3-Trichlorobenzene	180	182

Additional Appendix IX Compounds And Their Quantitation Ions

Compound	Primary Quant Ions*	Secondary Quant Ions*
Acrolein	56	55,58
Bromoethane	108	-
Allyl chloride	41	78
Acrylonitrile	53	52,51
Chloroprene	53	51
Methacrylonitrile	41	39
Ethyl methacrylate	69	-
Methyl methacrylate	41	39
trans-1,4-Dichloro-2-butene	53	75
Vinyl acetate	43	86
Iodomethane	142	127
Vinyl acetate	43	86
2-Chloroethylvinyl ether	63	65

* Primary and secondary quantitation ions assigned by Laucks may be slightly different than those recommended in SW 846, in order to avoid interference.

APPENDIX XII

Target Analytes, Their Elution Order And Standard Mixes

Compound	Standard Mix
Dichlorodifluoromethane	6
Chloromethane	6
Vinyl Chloride	6
Bromomethane	6
Chloroethane	6
Trichlorofluoromethane	6
Acrolein	8
1,1-Dichloroethene	5
Acetone	7
Iodomethane	9
Bromoethane	10
Carbon disulfide	11
Allyl Chloride	12
Methylene chloride	5
trans-1,2-Dichloroethene	5
Acrylonitrile	13
1,1-Dichloroethane	4
Vinyl acetate	14
Chloroprene	15
2,2-Dichloropropane	4
cis-1,2-Dichloroethene	5
2-Butanone	7
Methacrylonitrile	12
Bromochloromethane	4
Chloroform	4
1,1,1-Trichloroethane	4
Carbon tetrachloride	4
1,1-Dichloropropene	3
1,2-Dichloroethane-d4 (surr)	18
Benzene	2
1,2-Dichloroethane	3

Compound	Standard Mix
Trichloroethene	3
1,2-Dichloropropane	3
Dibromomethane	4
Methyl methacrylate	12
Bromodichloromethane	5
2-Chloroethylvinyl ether	16
cis-1,3-Dichloropropene	3
Ethyl methacrylate	12
4-Methyl-2-pentanone	7
Toluene-d8 (surr)	18
Toluene	2
trans-1,3-Dichloropropene	3
1,1,2-Trichloroethane	3
Tetrachloroethene	4
1,3-Dichloropropane	3
2-Hexanone	7
Chlorodibromomethane	5
1,2-Dibromoethane	3
Chlorobenzene	1
1,1,1,2-Tetrachloroethane	3
Ethylbenzene	2
m,p-Xylene	1,2
o-Xylene	1
Styrene	2
Bromoform	4
Isopropylbenzene	1
4-Bromofluorobenzene (surr)	18
Bromobenzene	2
1,2,3-Trichloropropane	3
1,1,2,2-Tetrachloroethane	3
n-Propylbenzene	1
trans-1,4-Dichloro-2-butene	17
2-Chlorotoluene	1
4-Chlorotoluene	1
1,3,5-Trimethylbenzene	2
tert-Butylbenzene	1
1,2,4-Trimethylbenzene	2

Compound	Standard Mix
sec-Butylbenzene	1
1,3-Dichlorobenzene	1
1,4-Dichlorobenzene	1
p-Isopropyltoluene	2
1,2-Dichlorobenzene	1
n-Butylbenzene	2
1,2-Dibromo-3-chloropropane	3
1,2,4-Trichlorobenzene	2
Naphthalene	2
Hexachlorobutadiene	3
1,2,3-Trichlorobenzene	2

Key:

1 = Supelco VOC Mix 1
2 = Supelco VOC Mix 2
3 = Supelco VOC Mix 3
4 = Supelco VOC Mix 4
5 = Supelco VOC Mix 5
6 = Supelco VOC Mix 6
7 = Supelco TCL Mix 1
8 = From neat
9 = Supelco Single std
10 = Chem Service Single Standard
11 = Supelco single standard
12 = Supelco 8240B Mix 7
13 = Supelco single std
14 = Supelco single standard
15 = Neat Material
16 = Supelco Single standard
17 = Supelco Single standard
18 = Neat material

At the time of this writing, these are the current standard solutions used for the calibration standards. However, these standards may change due to Vendor supply or project-specific requirements.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8276

Determination of Semivolatile Organic Compounds by SW-846 Method 8270D

Revision history:

Number	Date
0	02/05/98
1	02/17/99
2	04/25/00

Controlled Document

No. 20 **Assigned to:** Tetra

Revised by: Monica Carr, Organic Division Manager Date: 4/28/00

Approved by: Harry Romberg, QA Officer Date: 04-28-2000

Approved by: Kathy Kreps, Laboratory Director Date: 04-28-2000

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method is used for the determination of semivolatile organic analytes in aqueous, soil, sediment, and other matrices. This SOP follows SW-846 Method 8270D except for the specific deviations listed below or outlined in a project's specific QAPP.

1.1.2 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas/liquid/chromatography/mass spectroscopy and in the interpretation of chromatograms and mass spectra. Each analyst performing this method must have demonstrated the ability to perform the described chromatographic analysis and/or data interpretation.

1.2 Method Deviations & Comments

1.2.1 The following items represent deviations and comments of Method 8270D, as published, which are followed as standard operating procedure in the performance of this method at Laucks:

1.2.1.1 Method 3640A (Gel Permeation Chromatography cleanup) is utilized routinely for all soil/sediment sample extracts. GPC cleanup is performed on aqueous sample extracts as deemed necessary.

1.2.1.2 The initial calibration has been increased from five to six concentration levels in order to demonstrate linearity for all target analytes and to provide a low-level standard that will act as the reporting limit as outlined in the method.

1.2.1.3 The concentration of internal standards added to all sample extracts and calibration standards has been decreased from 40 ng/µL per compound to 20 ng/µL in order to accommodate 2 µL injection volumes as allowed by the method. This adjustment keeps the total nanograms injected the same and prevents overloading the analytical column.

1.2.1.4 Lauck's uses a relative response factor for all analytes. The method specifies that if the average RSD of all analytes for the initial calibration is ≤15%, then the RRF may be used for individual analytes with RSDs >15%. This method option will be used if any analyte's RSD exceeds 15% in the initial calibration. However, Laucks uses an internal guideline of 40 percent as an upper limit.

1.2.1.5 CLP Statement of Work, OLM03.1, DFTPP tuning criteria has been substituted as allowed by the method. Tuning criteria are listed in Appendix II.

1.2.1.6 All standards are stored at less than -10°C or by the manufacturer's recommendation. Sample extracts are stored at 4°C ±2°C.

1.2.1.7 The surrogate and matrix spikes will be added to the sample such that the final amount injected from normally concentrated samples is 100 ng for the base/neutral compounds and 150 ng for the acids. Acids will not be injected at 200 ng per injection to prevent exceeding the highest calibration standard of 160 ng.

1.3 Sample Collection, Sample Storage, Holding Times

1.3.1 Samples are normally collected in glass containers with Teflon-lined caps. All samples and sample extracts are stored at 4°C ± 2°C. Water samples must be extracted within 7 days of collection. Soil samples must be extracted within 14 days of collection. All sample extracts must be analyzed within 40 days of sample preparation.

1.4 Definition of Terms

1.4.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

Method Blank Spike	A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts or target analytes and surrogates are added each time sample extracts are prepared. Blank spikes are required on all HAZWRAP and NFESC work. In the context of this SOP, a blank spike is the same as a QC check standard.
CCC	Calibration Check Compound. A compound of analytical interest whose RRF in the CCV is compared to the average RRF from the initial calibration. The % difference must be less than the value specified in the method for the CCV to be considered valid. CCCs must also meet maximum %RSD criteria in an initial calibration.
CCV	Continuing calibration verification. This is the same acronym used in the CLP program. This is a standard injected at some prescribed frequency during the analysis sequence to determine whether the instrument has remained in calibration.
CLP	Contract Laboratory Program. The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In the context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.
DIW	Deionized water. Lab reagent water. Organic-free water. Since the systems used to provide DIW at Laucks all contain carbon polishing filters, they are capable of providing organic-free water for use in method blanks and method blank spikes.
IPCS	Instrument Performance Check Solution. A solution containing at a minimum DFTPP, pentachlorophenol, benzidine, and p,p'-DDT. The IPCS is analyzed at the start of a 12 hour QC period in order to verify DFTPP tuning criteria and evaluate column tailing factors. There are no specified tailing factor criteria in the published method, however, tailing factors should not exceed 4.0 .

Internal Standard	A compound added to every standard, blank, matrix spike, matrix spike duplicate, and sample extract at a know concentration, prior to analysis. Internal standards are used as the basis for quantitation of target compounds.
MDL	Method detection limit. The lowest concentration in a sample which will yield a positive result that is greater than zero at a known level of confidence. MDLs are empirically determined by Laucks.
MDL Standard	Method detection limit standard. A standard prepared so that the concentrations of the target analytes are approximately 4x the empirically determined MDLs on an extract basis. This standard is used to verify that the instrument is capable of detecting the target analytes on an ongoing basis.
QC Period	Quality control period. An analysis sequence initiated by the injection of one or more standards, followed by sample extracts. A QC period is 12 hours starting with the injection of the CCV standard or DFTPP performance evaluation.
RF	Response Factor. The measure of the mass spectral response of an analyte compared to its internal standard. Response factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples. RF is determined by the following equation:

$$RF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

where:

A_x - Area of target analyte primary ion
C_{is} - Concentration of internal standard
A_{is} - Area of internal standard primary ion
C_x - Concentration of target analyte

RSD or %RSD	Relative standard deviation or percent relative standard deviation. The ratio of the standard deviation of a set of values to the mean of the set of values. A measure of the similarity of the values one to another.
RT	Retention time. The time (in minutes) at which a target analyte elutes from the GC column.
Sequence	A set of sample extracts and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.
SPCC	System Performance Check Compound. A compound of analytical interest whose relative response factor (RRF) is monitored in the CCV for signs of chromatographic degradation. SPCCs generally have low RRFs and tend to decrease in response as the chromatographic system begins to deteriorate. They must meet a minimum RRF for initial and continuing calibrations.
EICP	Extracted ion current profile-a plot of ion abundance versus time (or scan number) for ion(s) of specified mass(es).
Surrogate	Compounds added to every standard, blank, matrix spike, matrix spike duplicate, and sample extract at a known concentration; used to evaluate extraction and analytical efficiency by measuring recovery. Surrogates are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental samples.

2. Equipment List and Standards

2.1 Chromatographic System

Gas Chromatograph:	Hewlett Packard 5890 I or II
Carrier Gas:	Helium 99.999% (ultra purity) or better
Column:	30 m x 0.25 mm x 0.25 μ capillary column (Restek RTX-5 or equivalent)
Automatic Sampler:	Hewlett Packard 7672A with 19405A and 3396A controllers
GC/MS Interface:	Capillary direct to the ion source of the mass spectrometer, fixed temperature

Mass Spectrometer:	Hewlett Packard 5970B
Data System:	Teknivent
Miscellaneous:	Assorted syringes, vials, caps, septa, injection port liners, ferrules, etc.
Note:	All of the above equipment may be substituted with equivalent or better equipment

2.2 Standards

2.2.1 Preparation of Semivolatile Standards

2.2.1.1 All standards prepared from this operating procedure must be logged into one of two standards preparation logbooks. One is maintained for stock solutions prepared from neat chemicals; the other is maintained for all working solutions. These logbooks are kept in the GC/MS semivolatile working area. When a standard is made, a solution number is assigned to it. This solution number is unique and will be used to track and identify the standard every time it is analyzed.

2.2.1.2 An example of the solution nomenclature used is a working ABN standard prepared on 11/13/91. The solution number assigned was MS 2-77-2. This label represents the following:

MS	Solution was made and used as a Mass Spec standard.
2	Solution was logged into standard book #2.
77	Page number on which solution has been recorded.
2	This denotes the second entry on page 77.

2.2.1.3 All standards must also be verified both qualitatively and quantitatively in order to satisfy EPA requirements for traceability. This may be accomplished by purchasing solutions which have been fully documented by a commercial vendor.

2.2.2 Preparation of Internal Standard Solution (ABN IS MIX @ 2000 ug/mL).

Internal standards
1,4-Dichlorobenzene-d4
Naphthalene-d8
Acenaphthene-d10
Phenanthrene-d10
Chrysene-d12
Perylene-d12

2.2.2.1 Commercially prepared and certified internal standard solution is purchased at a concentration of 2000 µg/mL and is used undiluted. This standard is monitored for degradation by evaporative losses. The standard should be replaced when the area counts increase more than 15% from when it was freshly opened. This standard is kept at -10°C until put into use. Once opened, the standard is kept at room temperature to avoid having the less soluble compounds fall out of solution. A new ampule of internal standard is used with a new CCV standard, which is prepared on a weekly basis.

2.2.3 Preparation of Surrogate Standards

Surrogate compounds
2-Fluorophenol
Phenol-d5
2-Chlorophenol-d4
2,4,6-Tribromophenol
1,2-Dichlorobenzene-d4
Nitrobenzene-d5
2-Fluorobiphenyl
p-Terphenyl-d14

2.2.3.1 Surrogate stock solutions are prepared by dissolving 100 mg of each analyte in 10 mL of methanol resulting in a stock solution with a concentration of 10,000 µg/mL. The one exception is p-terphenyl-d14 which is prepared by dissolving 50 mg in 10 mL of 50:50 benzene/methylene chloride for a final concentration of 5000 µg/mL.

2.2.3.2 An aliquot of each stock solution is diluted 1:200 (1:100 for p-terphenyl-d14) in methylene chloride and analyzed by the GC/MS department before they are incorporated into working solutions. The stocks must be within 80% - 120% of the expected value of 50 ng/µL to be considered usable.

2.2.3.3 5 mL of each of the base/neutral surrogate stock solutions (10 mL of the p-terphenyl-d14) and 7.5 mL of each of the acid surrogate solutions are mixed and diluted in methanol to a final volume of 500 mL to make a working solution of 100 µg/mL for the base/neutral surrogates and 150 µg/mL for the acid surrogates. An aliquot of the working solution is diluted 1:5 in methylene chloride and analyzed by the GC/MS department. The working solution must be within 80% - 120% of the expected values of 30 ng/µL for the acid surrogates and 20 ng/µL for the base/neutral surrogates before they are put into use by the extractions department.

2.2.3.4 Commercially prepared and certified surrogate solution may be purchased and used in place of the above described solutions at the discretion of the laboratory.

2.2.4 Preparation of Matrix Spike Standards

Matrix spike compounds
Phenol
2-Chlorophenol
1,4-Dichlorobenzene
N-Nitroso-di-n-propylamine
1,2,4-Trichlorobenzene
4-Chloro-3-methylphenol
Acenaphthene
2,4-Dinitrotoluene
4-Nitrophenol
Pentachlorophenol
Pyrene

2.2.4.1 Stock and working solutions of all matrix spike compounds utilized are prepared and verified in the same manner as surrogate standards. The final concentration of the acid compounds will be 150 µg/mL and the base/neutral compounds will be at a concentration of 100 µg/mL.

2.2.4.2 Commercially prepared and certified spiking solution may be purchased and used in place of the above described solution.

2.2.5 Preparation of DFTPP Solution

2.2.5.1 Prepare a solution of DFTPP (Decafluorotriphenylphosphine) at a concentration of 5000 µg/mL in acetone. Store this solution in amber screw-cap vials in the freezer. The vial in use may be stored at room temperature.

2.2.5.2 Commercially prepared and certified DFTPP solution may be purchased and used in place of the above described solution. This solution and working standards made from it are kept at -10°C.

2.2.6 Preparation of Calibration Standards

2.2.6.1 Calibration standards are prepared in methylene chloride from stock solutions which are purchased from a commercial source (e.g., Supelco or Restek). If an analyte required for calibration is not present in an available mixed solution, laboratory-prepared stock solutions which have been verified by GC/MS may be used. Laboratory prepared stock solutions should be tested against independent reference standards when they are available.

2.2.6.2 Calibration standards are prepared at six concentration levels (5, 10, 25, 40, 60 and 80 ng/µL). Each calibration standard contains all compounds of interest, surrogates, and internal standards. The internal standards are added so that they are present in all calibration standards at a concentration of 20 ng/µL each.

2.2.6.3 Through repetitive preparation of mixed semivolatile standards, it has been documented that benzidine is unstable when combined in working solutions with other semivolatile target compounds. Therefore, benzidine standards are prepared individually in the same manner as the multi-component stock and standard solutions.

2.2.7 Preparation of ABN200 stock solution

2.2.7.1 Assemble the following solutions in order to prepare a combined stock solution which will contain all analytes of interest at a concentration of 200 µg/mL each:

Analyte Mix	**Vendor**	**Stock #**	**Mix #** [(a)]
TCL Base-Neutrals Mix1	Supelco	#4-8900	(1)
TCL Base-Neutrals Mix2	Supelco	#4-8120	(2)
TCL Benzidines Mix	Supelco	#4-8906	(3)
TCL Hazardous Substances Mix1	Supelco	#4-8907	(4)
TCL Hazardous Substances Mix2	Supelco	#4-8908	(5)
TCL Phenols Mix	Supelco	#4-8904	(6)
TCL Polynuclear Aromatic Hydrocarbons Mix	Supelco	#4-8905	(7)
Acid Surrogate Mix	Supelco	#4-7261	(8)
B/N Surrogate Mix	Supelco	#4-7262	(9)
Pyridine	Supelco	#48305-U	(10)

(a) Refers to Appendix I standard solution information

Note: 1,2-diphenylhydrazine is detected as azobenzene. Azobenzene may be substituted for 1,2-diphenylhydrazine as it is in many commercially purchased calibration mixes.

Note: If performing additional analytes such as Appendix IX, the calibration stock and solutions are prepared separately. See Appendix IX of this SOP for details.

2.2.7.2 The vendor and catalog numbers provided are for reference only. Other vendor's certified solutions may be substituted.

2.2.7.3 Combine appropriate amounts of all solutions in a clean, silanized volumetric flask (10 mL capacity) so that all analytes are present at 200 µg/mL. Dilute to volume with methylene chloride, stopper the flask and mix well. Record all information in the working standards logbook and transfer the contents of the volumetric flask into silanized amber screw-cap vials. Store this solution in the freezer when not in use. The

vial must be marked with the logbook name, standard type, preparation date, solvent used, and expiration date.

2.2.8 Preparation of working calibration standards

2.2.8.1 To prepare working calibration standards, add the amounts listed below (in µL) of ABN200 stock solution, internal standard solution (ABN IS MIX @ 2000 ug/mL) and methylene chloride to clean vial inserts and use within one week.

	Amount of Standard ABN200 in µl	**Amount of Internal Standard in µl**	**Amount of CH_2Cl_2 in µl**
Working ABN 5	5	2	193
Working ABN 10	10	2	188
Working ABN 25	25	2	173
Working ABN 40	40	2	158
Working ABN 60	60	2	138
Working ABN 80	80	2	118

2.2.8.2 Log into the working solutions logbook all of the above information as the standards are made. Store all standards at less than -10°C for up to one week when not in use.

2.2.8.3 The working ABN 25 standard is made in larger quantity because it is used every day as a calibration check. It will be necessary to prepare a fresh ABN 25 on a weekly basis.

2.2.8.4 Calibration stock solutions which are received sealed in ampules from the manufacturer are useable up to their manufacturer's expiration date. The mixed ABN200 stock solution is stable for up to 6 months or 1 year when promptly ampuled. Working calibration standards may be used for 1 week.

3. Safety precautions

3.1 Routine Safety Precautions

3.1.1 All standards and sample extracts should be handled as if they are hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.4 Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.5 Almost all of the analytes under consideration are known or suspected carcinogens. Analysts should wash their hands after using any standard, solvent or sample extract. Additionally, a respirator should be worn or a fume hood utilized for extremely hazardous compounds or very dirty extracts.

3.2 Waste disposal

3.2.1 All waste solvents, expired standards and old extracts should be disposed of in the solvent waste can located in the prep area fume hood. Consult the laboratory SOP for more detail on waste disposal.

4. Operation procedures

4.1 Analytical Conditions

4.1.1 Chromatographic Conditions

Initial Temperature:	30°C
Initial Time:	4 minutes
Column Temperature Program:	8°C/minute
Final Temperature:	300°C
Final Time:	8 minutes
Injector Temperature:	275°C
Transfer Line Temperature:	280°C
Injector Purge Time Off:	42 seconds (0.7 minutes)
Injection Volume:	2 µL
Column Linear Velocity:	30-40 cm/sec (nominal 35 cm/sec measured at 30°C)

4.1.2 Mass Spectrometer Conditions

Electron Energy:	70 volts
Mass Range:	35 to 500 amu
Scan Time:	Not to exceed 1 second per scan
Scan Start Time:	4.5 minutes

4.2 Method Detection Limit Study

4.2.1 MDL studies are performed on an annual basis. This procedure is fully described in Laucks SOP on Determination of MDL's.

4.3 Method Reporting Limits

4.3.1 The method reporting limit for this method shall be set as described by method 8000B by using the lowest calibration standard as the method report limit. Values detected below this level will be reported but will be "J" flagged as outlined in Section 5.2 of this SOP.

4.4 Method Validation

4.4.1 Prior to the analysis of any samples, it is necessary to validate the method. A method validation study is performed in a similar manner to an MDL study with the exception that a minimum of 4 replicates are required and the concentration levels are typically higher. This procedure is fully described in Laucks SOP on Determination of QC limits.

4.5 Daily Instrument Maintenance

4.5.1 Daily instrument maintenance is required for good chromatography and proper calibration. The following steps must be undertaken as needed before the analysis of any standards or samples.

- Cool GC oven to 30°C
- Check background
- Remove injector septum and liner
- Remove column from injector
- Install a clean quartz liner
- Reinstall O-ring or replace if worn
- Install a new ferrule on the column
- Clip off 8-10 cm of the column. Check for proper cut
- Reinstall column in injector and adjust height
- Install injector cap and a new septum
- Clean and re-install the autosampler syringe
- Check the background again
- If background is okay, ramp the GC oven twice from 30°C to 300°C at 15°C/minute and hold 8 minutes

4.6 Instrument Tuning

4.6.1 The HP 5970B mass spectrometer uses FC-43 (PFTBA) as a mass calibration compound. Each instrument will require different ion ratios to pass the required DFTPP performance criteria. See Appendix II for the DFTPP tuning criteria. The following ratios are therefore approximate. Use manual tuning to tune the mass spectrometer.

Ion	% of ion 69
69	100%
131	25-35%
219	25-35%
414	1-3%

4.6.2 Ion peak widths should be in the 0.5 to 0.6 amu range. Excessive peak width can lead to loss of minor isotope peaks. Insufficient peak width can result in the loss of sensitivity. Ions for water, nitrogen, and oxygen should be <5% of ion 69. A copy of the PFTBA spectrum and tabular listing should be kept with the instrument historical file.

4.7 Initial Multi-Point Calibration

4.7.1 An instrument performance check solution containing DFTPP should be injected first in order to verify DFTPP tuning criteria, degradation, and column tailing factors. The spectrum of DFTPP must pass tuning criteria before any other standards are injected. Retuning of the instrument may be necessary to achieve this. Additionally, the DFTPP spectrum should be well within the performance criteria - i.e., no ion abundance should be borderline and the ratios should be routinely reproducible to insure a stable calibration.

4.7.2 The first option is to begin with the simplest approach, the linear model through the origin using RSDs, as described in section 7.5 of 8000B. In methods where this method is not appropriate, because the calibration acceptance criteria cannot be met, the next option of calibration (linear regression) is used. This calibration option is typically used in fuels because of the elevated response obtained in these analyses. The requirements for the linear regression model is that R^2 be greater than or equal to 0.99. The more complex calibration option is use of the quadratic curve. This calibration option requires a minimum of 6 points and is used in cases where the detector doesn't meet calibration criteria over a wide range. The difficulty with the quadratic is that the intercept may be greater than the detection limit. This calibration option exhibits a greater accuracy in the mid-range, and may demonstrate more extreme responses at the low and high end of the calibration, and therefore, it is important to dilute samples and extracts so that they are in the mid-range of the calibration.

4.7.3 For linear calibrations using the RSD, analyze standard solutions using a minimum of 5 different concentration levels. (Six calibration levels are typically used for 8270D.) The lowest concentration should establish the reporting limit. The highest concentration should define the upper usable working range of the detector. Criteria for evaluating these standards are detailed in Section 6.

4.8 Continuing Calibration Verification

4.8.1 At the beginning of a QC period, analyze an instrument performance check solution. The DFTPP tuning criteria in Appendix II must be met prior to analyzing a CCV standard. If DFTPP tuning criteria are met, analyze a CCV standard. The standard analysis must meet the %D and minimum RRF criteria detailed later in this SOP.

4.9 Sample Analysis

4.9.1 Analysis sequence

4.9.1.1 In general, the method blank accompanying the samples is injected prior to the analysis of the samples. This is not a requirement, however. Samples are then injected until the end of the 12 hour clock. After 12 hours have expired, instrument maintenance is performed and another IPCS and CCV standard are analyzed and evaluated before sample analysis continues.

4.9.2 Extract Preparation

4.9.2.1 Remove sample extracts from the refrigerator and allow them to come to room temperature.

4.9.2.2 Transfer 200 µL of extract to a vial insert.

4.9.2.3 Add 2 µL of IS solution (ABN IS MIX @ 2000 ug/mL).

4.9.2.4 Cap the vial and mix well.

4.9.2.5 Place the vial onto the autosampler for analysis.

4.9.2.6 For dilutions, decide what dilution is necessary from previous data or analyst judgment. Make dilution and then add 2 µL of IS solution prior to capping vial. Mix well prior to analysis.

4.9.3 Compound Identification

4.9.3.1 Compounds are tentatively identified if a peak elutes within 0.5 minute of that compound in the CCV standard. In addition, the internal standard for that compound should also be within 0.5 minute of its counterpart in the CCV standard. To confirm the presence of that compound in the sample extract, the mass spectrum of the peak must be evaluated. Spectra are compared against standard spectra of each compound generated on the instrument used for analysis.

4.9.3.2 The following criteria are used to evaluate mass spectra.

4.9.3.2.1 The intensities of the characteristic ions of a compound maximize within one scan of each other. Searches performed based on the presence of a target compound at a compound-specific retention time will be accepted as meeting this criterion.

4.9.3.2.2 All ions present in the standard mass spectra at a relative intensity greater than 30% (most abundant ion in the spectrum equals 100%) or the three ions of greatest intensity must be present in the sample spectrum.

4.9.3.2.3 The relative intensities of ions specified must agree within 30% between the standard and sample spectra. Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 20 and 80 percent.

4.9.3.2.4 If a compound cannot be verified by all of these criteria, but in the technical judgment of the analyst, the identification is correct, then report that identification and proceed with quantification.

4.9.3.2.5 The experienced analyst's judgment weighs heavily in evaluating chromatograms and mass spectra for compound identification. For instance, the retention times of surrogate compounds may be outside their expected windows due to sample matrix effects. If this has occurred, it must be fully documented in the appropriate report notes.

4.9.4 Common Analytical Problems

4.9.4.1 An analyst's professional judgment plays a large role in how data is interpreted. The following guidelines should be followed in order to facilitate consistency between analysts. Any anomalies not addressed in this SOP must be discussed with the supervisor prior to implementation. All anomalies and corrective actions must be documented.

4.9.5 Carryover

4.9.5.1 In some cases, if analytes in a sample are very high, there may be carryover from one analysis to the next. If a sample is suspected of being high due to historical data or extract color, the sample should be diluted prior to analysis, or one or more blanks should be analyzed after the sample to insure that there is no carryover between analyses.

4.9.5.2 However, in the case where high levels were not expected, and do appear in a sample analysis, the analysis after it should be examined carefully for carryover. Any sample analyte whose concentration exceeds 250 ng/µl in the extract should be considered a candidate for carryover.

4.9.5.3 If the following sample has no detected amount of the analyte or analytes which exceeded 250 ng/µl in the previous sample analysis, the following sample does not need to be re-analyzed.

4.9.5.4 If the following sample has detected amounts of the analyte or analytes which exceeded the 250 ng/µl in the previous sample analysis, the sample must be re-analyzed to test for possible carryover.

4.9.6 Manual Peak Integrations

4.9.6.1 Manual peak integrations should be used only when necessary to correct for matrix interference, tangent peaks, and rising baselines. Manual integrations are not to be used in an attempt to meet calibration, surrogate recovery, or spike recovery criteria.

4.9.6.2 If the chromatogram shows degradation due to sample loading e.g. split peaks, lift off, or severe tailing, the sample should be diluted and reanalyzed if required detection limits permit.

4.9.6.3 If a manual integration is necessary, use the following guidelines:

- Integrate only the peak. Start where the peak lifts from the baseline and end as soon as it returns to the baseline. Do not integrate extra baseline in an attempt to increase peak area.
- Do not "peak shave". Do not cut off legitimate parts of the peak in order to reduce peak area.
- In cases of tangent skims, do not increase or decrease peak areas or heights by skimming extra long baselines or drawing the baseline too low.

- Always initial and date your manual integrations.

4.9.7 Compound Quantification

4.9.7.1 Target compound concentrations are calculated using the following equations:

4.9.7.2 Aqueous samples

4.9.7.2.1 The equation for internal standard calculations is

$$Extract\ Concentration(ng / \mu L) = \frac{A_x \times C_{is}}{A_{is} \times RF_{average}}$$

where:

A_x	= Response for the target analyte
A_{is}	= Response for the internal standard
C_{is}	= Concentration of internal standard, in ng/µL
$RF_{average}$	= Average Response Factor (calculated from the initial calibration)

4.9.8 If the %RSD of a compound's relative response factor is 15% or less, than the concentration may be determined using the average response factor from the initial calibration. Alternatively, the RF may be used as long as the average RSD of all calibration analytes is ≤15%. Laucks uses 40% percent as the upper limit for all compounds as an internal guideline although it is not a requirement of SW 846.

4.9.8.1.1 The above equation is used directly by the HP computer to yield the extract concentration.

4.9.8.1.2 To calculate the actual sample concentration, the following calculation must be used.

$$Sample\ Concentration(\mu g / L) = \frac{F \times D \times V_f \times GPC}{V_i}$$

where:

F	= Amount found from HP quantitation report (ng/µL)
D	= Dilution factor of extract
V_f	= Final extract volume (µL)
GPC	= GPC dilution factor. Use 1 if GPC was not performed, 2 if GPC was used

V_i = Initial sample volume (mL)

4.9.8.1.3 Any sample extracts which exceed the upper calibration range for any analyte of interest must be diluted and reanalyzed to bring the analyte into the working range of the calibration.

4.9.8.2 Non-aqueous samples

4.9.8.2.1 The results calculation for non-aqueous samples is very similar to that for aqueous samples. The only difference is the inclusion of a total solids term to calculate the dry weight equivalent of the initial sample size.

$$Sample\ Concentration(\mu g / L) = \frac{F \times D \times V_f \times GPC}{W_s \times T_s}$$

where:

W_s = Sample size extracted in grams.
T_s = Total Solids in decimal format (i.e. 0.76 not 76).

4.9.8.2.2 Any sample extracts which exceed the upper calibration range for any analyte of interest must be diluted and reanalyzed to bring the analyte into the working range of the calibration.

5. Reports

5.1 Data Packet Organization

5.1.1 See Appendix III for a check list detailing data packet organization.

5.2 Quality Control Reports

5.2.1 All results for quality control tests are entered into the lab data base. Printouts of all data entered must be included in the data packet. The routine minimum is a method blank report, a method blank spike report, and an MS/MSD report.

5.3 Sample Result Reports

5.3.1 Data Qualifying Flags

5.3.1.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

U: The analyte of interest was not detected, to the limit of detection indicated.

B: The analyte of interest was detected in the method blank associated with the sample, as well as in the sample itself. The B flag is applied without regard to the relative concentrations detected in the blank and sample.

J: The analyte of interest was detected below the practical quantitation limit. This value should be regarded as an estimate.

D: The value reported is derived from the analysis of a diluted sample or sample extract.

X: Indicates an unresolvable isomeric pair. This flag indicates that calculated results are the sum of the two isomers.

E: The value reported is based on a sample or sample extract in which the target analyte concentration exceeded the calibration range. The value reported should be considered an estimate.

6. Quality Control

6.1 General Issues

6.1.1 See Appendix VII and VIII for QA/QC limit and corrective action tables.

6.2 Initial Calibration

6.2.1 Criteria

6.2.1.1 Initial calibration data are evaluated using %RSD of the relative response factors as well as minimum average RRFs. The %RSD must be < 30% for each individual Calibration Check Compound (CCC). All other RRFs must be ≤15%. Alternatively, RRFs may be used as long as the average RRFs for all compounds in the method are ≤15% and the CCCs are <30%. Laucks uses an internal guideline of 40% as an upper control limit for each compound.

6.2.1.2 Calculate the %RSD for all compounds. CCC criteria are listed in Appendix IV.

6.2.1.3 Calculate the individual and average RFs for each compound.

6.2.1.4 RFs are calculated using the equation

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Response of target analyte
A_{is} = Response of internal standard
C_s = Amount of target analyte (ng/µL)
C_{is} = Amount of internal standard (ng/µL)

6.2.1.5 The minimum acceptable average RF for all analytes is 0.050. See Appendix IV for a listing of all SPCCs.

6.2.2 Corrective action

6.2.2.1 If the criteria are not met, other standards may be analyzed or appropriate instrument maintenance and analysis of new standards must be performed. Failure to achieve the required minimum average RRF for the SPCC compounds may indicate the need to perform instrument maintenance or prepare fresh calibration standards.

6.2.2.2 Some compounds, including but not limited to the nitroanilines, the nitrophenols and some additional Appendix IX analytes, tend to show poor or erratic response at the lower calibration levels.

6.2.2.2.1 For routine analyte lists the lowest standard may be omitted from the initial calibration as long as the %RSD does not exceed 30% for any which are CCCs. Additionally, those compounds which are omitted from the lower calibration levels will also have an elevated reporting level to that of the lowest standard.

6.2.2.2.2 For the Appendix IX analytes which exhibit odd calibration behavior refer to Appendix XII for details on calibration.

6.3 Continuing Calibration Verification

6.3.1 Criteria

6.3.1.1 At the beginning of each 12 hour QC period, a CCV standard is analyzed. The RF for each compound is calculated and the percent difference is calculated as follows:

$$\%Difference = \frac{RF_c - RF_i}{RF_i} \times 100$$

where:

RF_i = Average RF from Initial Calibration.
RF_c = RRF from CCV standard.

6.3.2 The %D results for all CCCs must be less than 20%. Laucks uses 40% percent as the upper limit for all compounds as an internal guideline although it is not a requirement of SW 846.

6.3.2.1 In addition, all compounds must have a minimum RRF of at least 0.050. See Appendix V for all CCV criteria.

6.3.3 Corrective action

6.3.3.1 Check that all peaks have been properly integrated. Check the calculations. If the %D criteria are still not met, perform corrective instrument maintenance or re-tuning, and reanalyze the standard. If the %D or minimum RF criteria are still not met, a new CCV standard may need to be prepared, a new initial calibration performed, a new column installed, or other instrument maintenance performed in order to meet the CCV criteria.

6.4 Method Blank

6.4.1 Criteria

6.4.1.1 A method blank is used to verify contamination-free reagents and apparatus. A method blank is prepared with every set of samples extracted at the same time, at a frequency of at least one blank per 20 samples.

6.4.1.2 Laucks criteria for a method blank is less than one-half the RL for each analyte, or less than 5 percent of the regulatory limit associated with that analyte, or less than 5 percent

of the sample result for the same analyte, whichever is greater for the method blank to be acceptable.

6.4.1.3 Since phthalate compounds are common laboratory contaminants, these compounds are allowed to be present in a method blank at the RL before corrective action is required. Any analyte response above the MDL is reported. Values below the reporting limit are "J" flagged. Method blank control limits are detailed in Appendix VI.

6.4.1.4 Where contractually required, all analyte concentrations in the method blank must be <MDL.

6.4.2 Corrective action

6.4.2.1 When this criteria is exceeded, corrective action shold be taken to find/reduce/eliminate the source of this contamination in the method blank. Sample corrective action may be limited to qualification for blank contamination. When the concentrations of any target analytes within the method blank are above one-half of the reporting limit for the majority of target analytes or above the reporting limit for target analytes known to be common laboratory contaminants, the effect this may have had on the samples will be assessed. If any analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps shall be taken to find/reduce/eliminate ths source of this contamination in the method blank. The case narrative should also discuss the situation. If an analyte is found in the method blank and some, or all, of the other batch samples, additional corrective action is required to reanalyze the method blank, and any samples containing the same contaminant. If the contamination remains, the contaminated samples of the batch would be reprepared and reanalyzed with a new method and batch specific QC samples. Sporadic cases of contamination may be difficult to control, however, daily contamination would not be acceptable.Out-of-control surrogate recoveries in the method blank require reanalysis of the method blank.

6.4.3 Documentation

6.4.3.1 Copies of all method blank analyses are stored with the sample analyses raw data. In addition, the raw data for the method blank analyses are stored in the laboratory for an extended period of time. The results for the method blank analyses are reported electronically via the laboratory's LIMS database. If criteria are not met, reanalysis of additional blank(s) are noted in the instrument run log. Outliers are discussed in the case narrative.

6.5 QC Check Sample (LCS)

6.5.1 Criteria

6.5.1.1 The LCS is used to determine whether a method is in control during sample preparation and analysis. A LCS follows the same protocol as the matrix spike analysis except that the spiking solution is added to a blank matrix (deionized water for water or sea sand for soil/sediments) instead of an actual sample. It is recommended that all target analytes of concern be spiked into the LCS. A subset of the single-component target analytes can be substituted for the full list if specified in project-specific contracts or workplans per the USACOE Shell document.

6.5.2 Corrective action

6.5.2.1 Check all peak integrations and sample calculations.

6.5.2.2 If the analyte recoveries still exceed the control limits, the blank spike extract should be reanalyzed.

6.5.2.3 If the analyte recoveries are still out of control, re-extraction of the associated samples is required.

6.6 Matrix Spike

6.6.1 Criteria

6.6.1.1 A sample is chosen from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to extraction. It is not required that a matrix spike analysis be performed with each extraction batch unless the project QAPP requires it. However, the minimum frequency for MS analysis is 1 each per 20 samples per matrix. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of selected target analytes.

6.6.1.2 Analyte recovery is calculated as follows:

$$\%Recovery = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Concentration in spiked sample.
SR = Native concentration in unspiked sample.
SA = Concentration of spike added.

6.6.1.3 MS recovery control limits are empirically derived from Lauck's data and can be found in the Laucks QC Limits database.

6.6.2 Corrective action

6.6.2.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action may involve recalculation, re-extraction, and/or reanalysis. This process should also look at the recovery of surrogate compounds in the MS sample and at the recovery of matrix spiking compounds from the extraction batch blank spike analysis. In all cases, a narrative explanation of the condition is required to detail the corrective actions taken.

6.6.2.2 If any analyte recovery exceeds the control limits the following action must be taken:

6.6.2.2.1 If the blank spike analysis yielded recoveries outside the control limits then re-extract and reanalyze all samples extracted with the MS/MSD

6.6.2.2.2 If the blank spike analysis was in control then recoveries outside the control limits can be attributed to matrix effect and sample results are processed as normal. The report comments or narrative section must include comments about the out-of-control recoveries.

6.7 Matrix Spike Duplicate

6.7.1 Criteria

6.7.1.1 The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used to measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values.

6.7.1.2 The calculation for RPD is as follows:

$$RPD = \frac{S1 - S2}{(S1 + S2)/2} \times 100$$

where:

S1 = Measured concentration for MS sample.
S2 = Measured concentration for MSD sample.

RPD control limits are detailed in Laucks QC Control Limits database.

6.7.2 Corrective action

6.7.2.1 Corrective action for RPD values which exceed the control limits follows the corrective action for MS/MSD recoveries. If more than one RPD exceeds the control limit, re-extraction may not be required if it can be demonstrated that the sample is non-homogeneous and all MS/MSD recoveries are within the control limits.

6.8 Surrogate Recovery

6.8.1 Criteria

6.8.1.1 Surrogates are chemically similar compounds added to every sample, method blank and QC sample prior to sample processing. They are used to monitor for potential sample processing errors and matrix effects.

6.8.1.2 Surrogate compound recoveries are calculated as follow:

$$\%Recovery = \frac{S_m}{S_a} \times 100$$

where:

S_m = Concentration of surrogate measured in extract.
S_a = Concentration of surrogate added.

6.8.1.3 Surrogate recovery control limits are tabulated in the Laucks QC Control Limits database, NEW_TEST.

6.8.2 Corrective Action

6.8.2.1 Check calculations for possible error.

6.8.2.2 Check instrument performance, if necessary correct the problem and re-analyze the extract.

6.8.2.3 Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant matrix interference. This may result in the dilution of the surrogate response to the point that the recoveries can not be measured. If the surrogate recoveries are available from a less-diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the QC limits, and no further action is required. For all package work both the diluted and undiluted analyses will be provided.

6.8.2.4 Re-extraction is not necessary in the case where a sample is chosen for MS/MSD analyses and the same recovery pattern is present in all three analyses. In this case, matrix effects may be assumed and re-extraction is not required for this sample.

6.8.2.5 If only one fraction is being analyzed for and surrogates that relate to the other fraction are out-of-control, then re-extraction and reanalysis for the target fraction is not required.

6.8.2.6 All other circumstances require re-extraction and reanalysis of the affected sample(s).

6.8.2.7 Out of control surrogate recoveries in the method blank require that all the samples in the associated batch be re-extracted and reanalyzed. In any case, it is imperative to identify the problem associated with low recovery so that it can be corrected. It is a

requirement that all out of control surrogate recoveries and the corrective action taken be discussed in the narrative.

7. References

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 4th Edition, Method 8270D, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique," Revision 4, January 1998, U.S. EPA.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, 2nd Update, Method 3640A, "Gel-Permeation Cleanup," Revision 1, November 1992, US EPA.

US EPA. Contract Laboratory Program, Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, Document Number OLM03.1, August 1994.

APPENDIX I

Calibration Standard Solution Concentrations, ng/µL

Compound	STD1	STD2	STD3	STD4	STD5	STD6	Std. Mix#
Phenol	5	10	25	40	60	80	(6)
bis(2-Chloroethyl)ether	5	10	25	40	60	80	(1)
2-Chlorophenol	5	10	25	40	60	80	(6)
1,3-Dichlorobenzene	5	10	25	40	60	80	(2)
1,4-Dichlorobenzene	5	10	25	40	60	80	(2)
Benzyl Alcohol	5	10	25	40	60	80	(5)
1,2-Dichlorobenzene	5	10	25	40	60	80	(2)
2-Methylphenol	5	10	25	40	60	80	(4)
Bis(2-chloroisopropyl)ether	5	10	25	40	60	80	(1)
4-Methylphenol	5	10	25	40	60	80	(6)
N-Nitroso-di-n-propylamine	5	10	25	40	60	80	(1)
Hexachloroethane	5	10	25	40	60	80	(2)
Nitrobenzene	5	10	25	40	60	80	(2)
Isophorone	5	10	25	40	60	80	(2)
2-Nitrophenol	5	10	25	40	60	80	(6)
2,4-Dimethylphenol	5	10	25	40	60	80	(6)
Benzoic Acid	5	10	25	40	60	80	(4)
bis(2-Chloroethoxy)methane	5	10	25	40	60	80	(1)
2,4-Dichlorophenol	5	10	25	40	60	80	(6)
1,2,4-Trichlorobenzene	5	10	25	40	60	80	(2)
Naphthalene	5	10	25	40	60	80	(7)
4-Chloroaniline	5	10	25	40	60	80	(5)
Hexachlorobutadiene	5	10	25	40	60	80	(2)
4-Chloro-3-methylphenol	5	10	25	40	60	80	(6)
2-Methylnaphthalene	5	10	25	40	60	80	(5)
Hexachlorocyclopentadiene	5	10	25	40	60	80	(2)
2,4,6-Trichlorophenol	5	10	25	40	60	80	(6)
2,4,5-Trichlorophenol	5	10	25	40	60	80	(4)
2-Chloronaphthalene	5	10	25	40	60	80	(2)
2-Nitroaniline	5	10	25	40	60	80	(5)
Dimethylphthalate	5	10	25	40	60	80	(1)
Acenaphthylene	5	10	25	40	60	80	(7)
2,6-Dinitrotoluene	5	10	25	40	60	80	(2)
3-Nitroaniline	5	10	25	40	60	80	(5)
Acenaphthene	5	10	25	40	60	80	(7)
2,4-Dinitrophenol	5	10	25	40	60	80	(6)

Compound	STD1	STD2	STD3	STD4	STD5	STD6	Std. Mix#
4-Nitrophenol	5	10	25	40	60	80	(6)
Dibenzofuran	5	10	25	40	60	80	(5)
2,4-Dinitrotoluene	5	10	25	40	60	80	(2)
Diethylphthalate	5	10	25	40	60	80	(1)
4-Chlorophenyl-phenylether	5	10	25	40	60	80	(1)
Fluorene	5	10	25	40	60	80	(7)
4-Nitroaniline	5	10	25	40	60	80	(5)
4,6-Dinitro-2-methylphenol	5	10	25	40	60	80	(6)
N-Nitrosodiphenylamine	5	10	25	40	60	80	(1)
4-Bromophenyl-phenylether	5	10	25	40	60	80	(1)
Hexachlorobenzene	5	10	25	40	60	80	(2)
Pentachlorophenol	5	10	25	40	60	80	(6)
Phenanthrene	5	10	25	40	60	80	(7)
Anthracene	5	10	25	40	60	80	(7)
Carbazole	5	10	25	40	60	80	(2)
Di-n-butylphthalate	5	10	25	40	60	80	(1)
Fluoranthene	5	10	25	40	60	80	(7)
Pyrene	5	10	25	40	60	80	(7)
Butylbenzylphthalate	5	10	25	40	60	80	(1)
3,3'-Dichlorobenzidine	5	10	25	40	60	80	(3)
Benzo(a)anthracene	5	10	25	40	60	80	(7)
Chrysene	5	10	25	40	60	80	(7)
bis(2-Ethylhexyl)phthalate	5	10	25	40	60	80	(1)
Di-n-octylphthalate	5	10	25	40	60	80	(1)
Benzo(b)fluoranthene	5	10	25	40	60	80	(7)
Benzo(k)fluoranthene	5	10	25	40	60	80	(7)
Benzo(a)pyrene	5	10	25	40	60	80	(7)
Indeno(1,2,3-cd)pyrene	5	10	25	40	60	80	(7)
Dibenzo(a,h)anthracene	5	10	25	40	60	80	(7)
Benzo(g,h,i)perylene	5	10	25	40	60	80	(7)
N-Nitrosodimethylamine	5	10	25	40	60	80	(1)
2-Fluorophenol	5	10	25	40	60	80	(8)
Aniline	5	10	25	40	60	80	(5)
Phenol-d5	5	10	25	40	60	80	(8)
2-Chlorophenol-d4	5	10	25	40	60	80	(8)
1,2-Dichlorobenzene-d4	5	10	25	40	60	80	(9)
Nitrobenzene-d5	5	10	25	40	60	80	(9)
2-Fluorobiphenyl	5	10	25	40	60	80	(9)
2,4,6-Tribromophenol	5	10	25	40	60	80	(8)

Compound	STD1	STD2	STD3	STD4	STD5	STD6	Std. Mix#
1,2-Diphenylhydrazine	5	10	25	40	60	80	(2)
Benzidine	5	10	25	40	60	80	(3)
Terphenyl-d14	5	10	25	40	60	80	(9)

APPENDIX II

DFTPP Tuning Criteria

Mass	Relative Abundance
51	30-80% of mass 198
68	less than 2% of 69
69	present
70	less than 2% of 69
127	25-75% of mass 198
197	less than 1% of 198
198	100%
199	5-9% of mass 198
275	10-30% of mass 198
365	greater than 0.75% of mass 198
441	0-100 % of mass 443
442	40-110% of mass 198
443	15-24% of mass 442

CLP requires that the three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of DFTPP. Do not background subtract part of the DFTPP peak.

SW 846 states that the following approach has been shown to be useful: the mass spectrum of DFTPP may be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of DFTPP. Do not background subtract part of the DFTPP peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceeded 20%. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 inches of the capillary column. The use of a guard column between the injection port and the analytical column may help prolong analytical column performance.

APPENDIX III

Data Packet Order List

QC Summary
Surrogate Recovery Summary Report
Blank Spike Recovery Report
MS/MSD Recovery Report
Method Blank Summary
GC/MS Instrument Performance Check
Internal Standard Area and RT Summary Report

Sample Data
Target Compound Results (Organics Analysis Data Sheet)
Tentatively Identified Compound (TIC) Results (if required)
Sample Chromatograms, quantitation reports and spectra for all samples

Standards Data
Initial Calibration Summary Report
Chromatograms and quantitation reports for all initial calibration standards
Continuing Calibration Summary Reports
Chromatograms and quantitation reports for all CCV Standards

Raw QC Data
Bar Graph Spectrum, mass listing and chromatogram for every DFTPP injection
Method Blank Data
Target Compound Results (Organics Analysis Data Sheet)
Tentatively Identified Compound (TIC) Results (if required)
Chromatograms, quantitation reports and spectra for all method blanks
Blank Spike Data
Target Compound Results (Organics Analysis Data Sheet)
Chromatograms, quantitation reports and spectra for all blank spikes
Matrix Spike/Matrix Spike Duplicate Data
Target Compound Results (Organics Analysis Data Sheet)
Chromatograms, quantitation reports and spectra for all MS analyses
Control Charts

Bench Sheets
All extraction bench sheets, analysis log book pages, chains of custody, and any other pertinent information

APPENDIX IV

Initial Calibration Criteria

Calibration Check Compound	%RSD Limit
Phenol	< 30%
1,4-Dichlorobenzene	< 30%
2-Nitrophenol	< 30%
2,4-Dichlorophenol	< 30%
Hexachlorobutadiene	< 30%
4-Chloro-3-methylphenol	< 30%
2,4,6-Trichlorophenol	< 30%
Acenaphthene	< 30%
N-Nitrosodiphenylamine	< 30%
Pentachlorophenol	< 30%
Fluoranthene	< 30%
Di-n-octylphthalate	< 30%
Benzo(a)pyrene	< 30%

System Performance Check Compound	Minimum Average RF
N-Nitroso-di-n-propylamine	0.050
Hexachlorocyclopentadiene	0.050
2,4-Dinitrophenol	0.050
4-Nitrophenol	0.050

Note: All analytes must have RFs 0.050.

APPENDIX V

Continuing Calibration Verification Criteria

Calibration Check Compound	%D Limit
Phenol	20%
1,4-Dichlorobenzene	20%
2-Nitrophenol	20%
2,4-Dichlorophenol	20%
Hexachlorobutadiene	20%
4-Chloro-3-methylphenol	20%
2,4,6-Trichlorophenol	20%
Acenaphthene	20%
N-Nitrosodiphenylamine	20%
Pentachlorophenol	20%
Fluoranthene	20%
Di-n-octylphthalate	20%
Benzo(a)pyrene	20%

System Performance Check Compound	Minimum RF
N-Nitroso-di-n-propylamine	0.050
Hexachlorocyclopentadiene	0.050
2,4-Dinitrophenol	0.050
4-Nitrophenol	0.050

Note: All analytes must have RFs 0.050.

APPENDIX VI

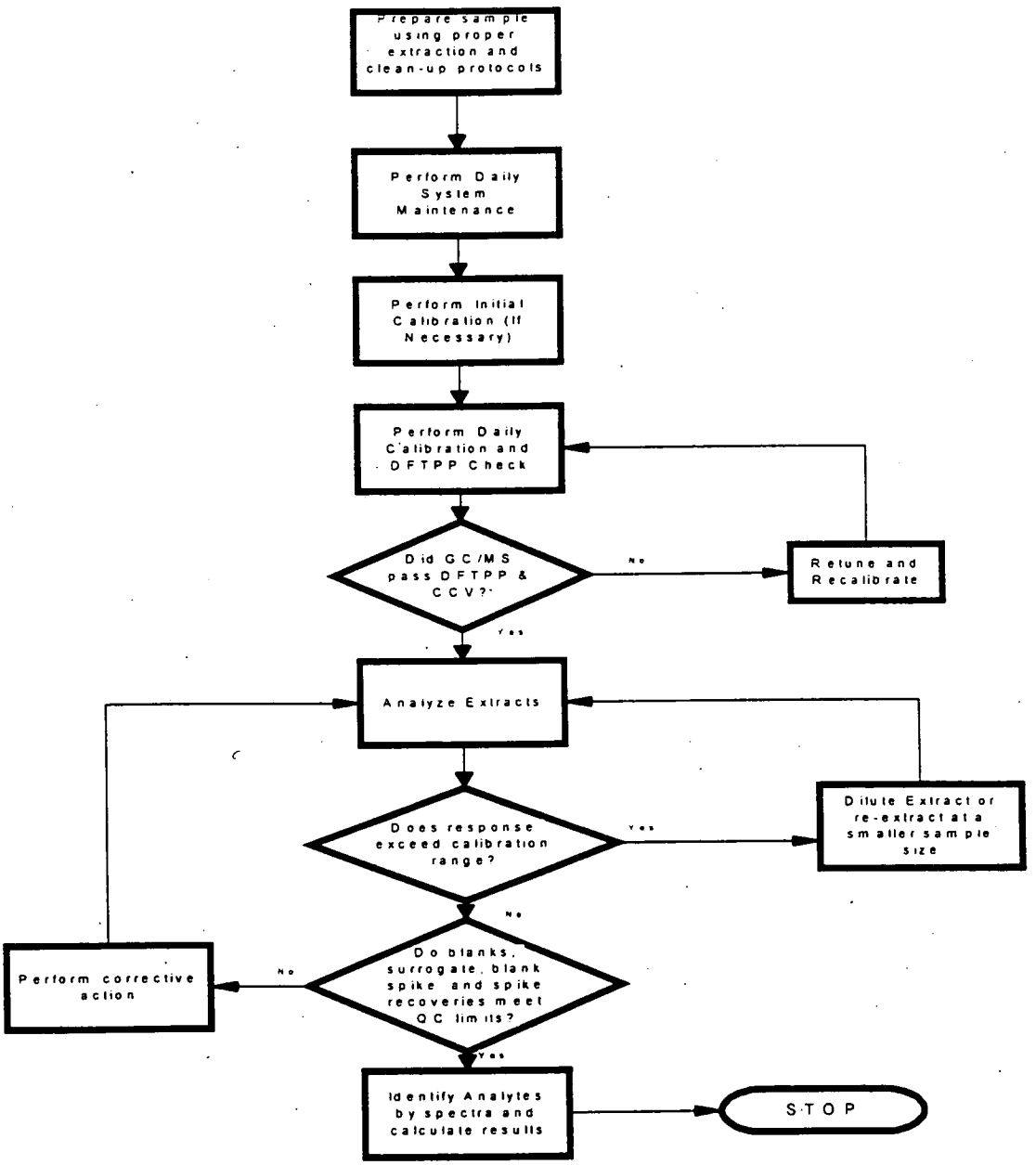
Method Blank Control Limits

Compound	Control Limits Water	Soil
Phthalates	RL	RL
All other compounds	1/2 RL	1/2 RL

If contractually required, all analyte concentrations must be < MDL in the method blank.

APPENDIX VII

Method 8270D Flow Chart



APPENDIX VIII

Method 8270D QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
DFTPP Tuning Verification (50 ng)	Mass Abundance 51 30-80% of 198 68 <2% of 69 69 present 70 <2% of 69 127 25-75% of 198 197 <1% of 198 198 100% 199 5-9% of 198 275 10-30% of 198 365 >.75% of 198 441 present but < 443 442 40-110% of 198 443 15-24% of 442	Mass Abundance 51 30-80% of 198 68 <2% of 69 69 present 70 <2% of 69 127 25-75% of 198 197 <1% of 198 198 100% 199 5-9% of 198 275 10-30% of 198 365 >.75% of 198 441 present but < 443 442 40-110% of 198 443 15-24% of 442	Every 12 hours: CLP Criteria is used as allowed by the method.	Retune instrument to pass criteria.	
Initial Calibration	Minimum of 5 levels, lowest near but above MDL. %RSD for CCC <30. All others should be <15%. RF for SPCC >0.05.	6 levels. %RSD for CCC <30. All others <15%. All RFs >0.05 Alternatively. average RSD must be <15% 40% as an upper limit.	At minimum. yearly or as necessary due to major instrument maintenance or continuing difficulties meeting the CCV requirements.	Re-analysis of out of control standards.	Copies of all raw data. mass calibration. tune, and Form VI.
Continuing Calibration Verification	Mid-level standard every 12 hours. %D <20% for CCCs SPCCs >0.05. IS Area must be -50% to +100% of the IS in the ICV. RT of IS must be within ±30 seconds of the RT of the IS in the IC.	25 ng/µl standard every 12 hours. %D for CCC<20. All RFs >0.05 Average %D must be <15%. 40% as an upper limit. IS Area must be -50% to +100% of the IS in the IC. No RT limits for IS in the CCV.	Every 12 hours.	Perform system maintenance, re-analyze CCV standard.	
Internal Standards	1.4-Dichlorobenzene-d4. Naphthalene-d8. Acenaphthene-d10. Phenanthrene-d10. Chrysene-d12. Perylene-d12. all @ 40 ng/uL ea..	1.4-Dichlorobenzene-d4. Naphthalene-d8. Acenaphthene-d10. Phenanthrene-d10. Chrysene-d12. Perylene-d12. all @ 20 ng/µl ea. Area must be -50% to + 100% of the area of the IS in the CCV. RT must be within 0.5 minutes of RT in CCV.	All standards. blanks. matrix spikes. matrix spike duplicates. blank spikes. SRMs. and sample re-extracts.	Re-analyze any sample which IS areas or RTs are out of range.	
Method Blank	Analytes must be <MDL except phthalates which must be <5X the MDL.	All analytes <1/2 RL. Except phthalates up to RL.	One method blank per 20 samples or each extraction batch of samples, whichever is more frequent.	Re-analyze blank. If still out of control. re-extract the entire batch of samples unless the offending analyte(s) are not detected in the associated samples.	Notation in instrument log and case narrative if applicable.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Surrogate Recovery	Nitrobenzene-d5. 2-Fluorobiphenyl. Terphenyl-d14. Phenol-d6. 2-Fluorophenol. & 2.4.6-Tribromophenol. Upper and lower recovery limits determined by 3X standard deviation of at least twenty samples. To be performed at least semi-annually.	Nitrobenzene-d5. 2-Fluorobiphenyl. Terphenyl-d14. Phenol-d6. 2-Fluorophenol. & 2.4.6-Tribromophenol. Upper and lower recovery limits determined by 3X standard deviation of at least twenty samples. To be performed at least semi-annually.	All samples. method blanks. LCSs. LESs.	Re-extraction of the sample is required if any surrogate is <10% recovery or 2 acid surrogates or 2 B/N surrogates are out of control. All surrogates must be in control in the method blank, otherwise all associated samples must be re-extracted. Where contractually required. e.g. Navy work. all surrogates must be within control limits.	Any out of control surrogates are to be documented in the instrument logbook and the job comments section or case narrative.
Blank Spike Recovery	MS/MSD Recovery criteria	Empirically derived from five or more blank spikes. QC limit equals 3X.	One per batch of twenty.	Re-extract batch unless MS/MSD is perfect.	Narrate in case narrative.
MS/MSD Recovery & RPD	Empirically derived from five or more MS/MSD pairs. QC interval equals 3X standard deviation.	Empirically derived from five or more MS/MSD pairs. QC interval equals 3X standard deviation.	One per batch of twenty.	Re-extract batch unless blanks spike is perfect or documentable matrix effect is present.	Narrate problems in case narrative.

APPENDIX IX

Appendix IX Calibration Standard Solution Concentrations, ng/µL

Compound	STD1	STD2	STD3	STD4	STD5	Std Mix #
2,6-Dichlorophenol	10	25	40	60	80	(A5)
1,2,4,5-Tetrachlorobenzene	10	25	40	60	80	(A2)
2,3,4,6-Tetrachlorophenol	10	25	40	60	80	(A5)
Dinoseb	10	25	40	60	80	(A5)
Methanesulfonate, methyl	10	25	40	60	80	(A6)
Methanesulfonate, ethyl	10	25	40	60	80	(A6)
Phosphorothiotic Acid	10	25	40	60	80	(A4)
Safrole	10	25	40	60	80	(A6)
Isosafrole, cis & trans	10	25	40	60	80	(A6)
1,4-Naphthoquinone	10	25	40	60	80	(A6)
1,3-Dinitrobenzene	10	25	40	60	80	(A6)
Thionazin	10	25	40	60	80	(A4)
2,4-D, methyl ester	10	25	40	60	80	(A4)
Diallate	10	25	40	60	80	(A4)
Phorate	10	25	40	60	80	(A4)
Dimethoate	10	25	40	60	80	(A4)
Silvex, methyl ester	10	25	40	60	80	(A4)
2,4,5-T, methyl ester	10	25	40	60	80	(A4)
Pronamide	10	25	40	60	80	(A6)
Disulfoton	10	25	40	60	80	(A4)
Methyl parathion	10	25	40	60	80	(A4)
Ethyl parathion	10	25	40	60	80	(A4)
Isodrin	10	25	40	60	80	(A6)
Chlorobenzilate	10	25	40	60	80	(A6)
Kepone	10	25	40	60	80	(A6)
Famphur	10	25	40	60	80	(A4)
3-Methylcholanthrene	10	25	40	60	80	(A6)
Ethanamine,N-methyl-N-nitroso	10	25	40	60	80	(A3)
N-nitrosomorpholine	10	25	40	60	80	(A3)
Butanamine, N-butyl-N-nitroso	10	25	40	60	80	(A3)
2-Naphthalenamine	10	25	40	60	80	(A3)
Diphenylamine	10	25	40	60	80	(A3)
1,3,5-Trinitrobenzene	10	25	40	60	80	(A3)
4-Aminobiphenyl	10	25	40	60	80	(A3)
Methyapyrilene, HCL	10	25	40	60	80	(A3)

Compound	STD1	STD2	STD3	STD4	STD5	Std Mix #
p-Dimethylaminoazobenzene	10	25	40	60	80	(A3)
2-Acetylaminofluorene	10	25	40	60	80	(A3)
7,12-Dimethylbenz(a)anthracene	10	25	40	60	80	(A3)
2-Picoline	10	25	40	60	80	(A7)
Pentachloroethane	10	25	40	60	80	(A7)
Acetophenone	10	25	40	60	80	(A7)
N-Nitrosopyrrolidine	10	25	40	60	80	(A7)
N-Nitrosopiperidine	10	25	40	60	80	(A7)
Hexachloropropene	10	25	40	60	80	(A7)
1,4-Phenylenediamine	10	25	40	60	80	(A7)
Pentachlorobenzene	10	25	40	60	80	(A7)
1-Naphthylamine	10	25	40	60	80	(A7)
5-Nitro-o-toluidine	10	25	40	60	80	(A7)
Pentachloronitrobenzene	10	25	40	60	80	(A7)
N-Nitroquinoline-N-oxide	10	25	40	60	80	(A7)
3,3-Dimethylbenzidine	10	25	40	60	80	(A7)
Hexachlorophene	10	25	40	60	80	(A7)
N-Nitrosodiethylamine	10	25	40	60	80	(A7)
o-Toluidine	10	25	40	60	80	(A7)
Phentermine	10	25	40	60	80	(A7)
Sulfotep	10	25	40	60	80	(A7)
Aramite	10	25	40	60	80	(A7)
Phenacetin	10	25	40	60	80	(A7)

Appendix X

Analytes Amenable to Analysis by Method 8270D

Current 8270D Target Analytes:

Compound	Primary Ion	Secondary Ion(s)	Retention Time (min)
Phenol	94	65, 66	12.20
bis(2-Chloroethyl)ether	93	63, 95	12.32
2-Chlorophenol	128	64, 130	12.33
1,3-Dichlorobenzene	146	148, 111	12.69
1,4-Dichlorobenzene	146	148, 111	12.87
Benzyl Alcohol	108	79, 77	13.44
1,2-Dichlorobenzene	146	148, 111	13.39
2-Methylphenol	107	108, 77	13.86
Bis(2-chloroisopropyl)ether	45	77, 121	13.88
4-Methylphenol	107	108, 77	14.33
N-Nitroso-di-n-propylamine	70	42, 101	14.39
Hexachloroethane	117	201, 199	14.27
Nitrobenzene	77	123, 65	14.64
Isophorone	82	195, 138	15.42
2-Nitrophenol	139	109, 65	15.59
2,4-Dimethylphenol	122	107, 121	15.89
Benzoic Acid	122	105, 77	16.62
bis(2-Chloroethoxy)methane	93	95, 123	16.16
2,4-Dichlorophenol	162	164, 98	16.34
1,2,4-Trichlorobenzene	180	182, 145	16.55
Naphthalene	128	129, 127	16.71
4-Chloroaniline	127	129, 65	17.04
Hexachlorobutadiene	225	223, 227	17.32
4-Chloro-3-methylphenol	107	144, 142	18.65
2-Methylnaphthalene	142	141	18.87
Hexachlorocyclopentadiene	237	235, 272	19.61
2,4,6-Trichlorophenol	196	198, 200	19.91
2,4,5-Trichlorophenol	196	198, 97	20.02
2-Chloronaphthalene	162	127, 164	20.39
2-Nitroaniline	65	92, 138	20.92
Dimethylphthalate	163	194, 164	21.68
Acenaphthylene	152	151, 153	21.71
2,6-Dinitrotoluene	165	63, 89	21.88

Current 8270D Target Analytes:

Compound	Primary Ion	Secondary Ion(s)	Retention Time (min)
3-Nitroaniline	138	108, 92	20.92
Acenaphthene	154	153, 152	22.32
2,4-Dinitrophenol	184	63, 154	22.59
4-Nitrophenol	139	109, 65	22.92
Dibenzofuran	168	139	22.83
2,4-Dinitrotoluene	167		23.08
4-Nitroaniline	138	65, 108	24.27
4,6-Dinitro-2-methylphenol	198	51, 105	24.39
N-Nitrosodiphenylamine	169	168, 167	24.45
4-Bromophenyl-phenylether	248	250, 141	25.51
4-Chlorophenyl-phenylether	204	206, 141	23.99
Fluorene	166	165, 167	23.92
Diethylphthalate	149	177, 150	23.95
Hexachlorobenzene	284	142, 249	25.93
Pentachlorophenol	266	264, 268	26.54
Phenanthrene	178	179, 176	26.94
Anthracene	178	176, 179	27.07
Carbazole	167	84	27.67
Di-n-butylphthalate	149	150	29.10
Fluoranthene	202	101	30.74
Pyrene	202	200, 203	31.42
Butylbenzylphthalate	149	91	33.82
3,3'-Dichlorobenzidine	252	254, 126	35.33
Benzo(a)anthracene	228	229, 226	35.27
Chrysene	228	226, 229	35.41
bis(2-Ethylhexyl)phthalate	149	167, 279	35.74
Di-n-octylphthalate	149	167, 43	37.57
Benzo(b)fluoranthene	252	253, 125	38.54
Benzo(k)fluoranthene	252	253, 125	38.63
Benzo(a)pyrene	252	253, 125	39.55
Indeno(1,2,3-cd)pyrene	276	138, 227	43.87
Dibenzo(a,h)anthracene	278	139, 279	43.99
Benzo(g,h,i)perylene	276	138, 277	45.12
N-Nitrosodimethylamine	74	42	5.76
2-Fluorophenol	112	64	9.46
Aniline	93	66, 65	12.08

Current 8270D Target Analytes:

Compound	Primary Ion	Secondary Ion(s)	Retention Time (min)
Phenol-d5	99	42, 71	12.17
2-Chlorophenol-d4	132	68	12.29
1,2-Dichlorobenzene-d4	152	115	13.36
Nitrobenzene-d5	82	128, 54	14.58
2-Fluorobiphenyl	172	171	20.16
2,4,6-Tribromophenol	330	332, 141	24.77
1,2-Diphenylhydrazine	77	182, 105	24.48
Benzidine	184	92, 185	31.27
Terphenyl-d14	244	122, 212	32.06

Current Appendix IX Analytes:

Compound	Primary Ion	Secondary Ion(s)	Retention Time (min)
2,6-Dichlorophenol	162	164, 63	16.02
1,2,4,5-Tetrachlorobenzene	216	214, 218	18.48
2,3,4,6-Tetrachlorophenol	230	232, 234	22.32
Dinoseb	211	163, 117	26.11
Methanesulfonate, methyl	80	79, 95	8.27
Methanesulfonate, ethyl	109	97	10.17
Phosphorothiotic Acid	97	121, 198	15.22
Safrole	162	104, 131	17.69
Isosafrole, cis & trans	162	104, 131	19.31
1,4-Naphthoquinone	158	102, 104	19.96
1,3-Dinitrobenzene	168	76, 122	20.63
Thionazin	97	96, 107	23.10
2,4-D, methyl ester	199	175, 234	23.55
Diallate	86	234, 236	24.40
Phorate	260	231, 121	24.44
Dimethoate	87	93, 125	25.04
Silvex, methyl ester	196	225, 282	25.33
2,4,5-T, methyl ester	233	235, 268	25.75
Pronamide	173	175, 255	25.77
Disulfoton	88	274, 142	26.06
Methyl parathion	263	125, 109	27.25
Ethyl parathion	291	235, 186	28.53
Isodrin	193	195, 230	29.07

Current Appendix IX Analytes:

Compound	Primary Ion	Secondary Ion(s)	Retention Time (min)
Chlorobenzilate	139	251, 253	31.64
Kepone	272	274, 355	32.30
Famphur	218	125, 217	32.52
3-Methylcholanthrene	268	252, 253	39.26
Ethanamine,N-methyl-N-nitroso	42	88, 43	7.08
N-nitrosomorpholine	56	86, 116	13.06
Butanamine, N-butyl-N-nitroso	84	41, 57	16.99
2-Naphthalenamine	143	144, 115	21.99
Diphenylamine	169	168, 167	23.07
1,3,5-Trinitrobenzene	213	75, 74	24.23
4-Aminobiphenyl	169	168, 170	25.02
Methyapyrilene, HCL	58	97, 191	28.52
p-Dimethylaminoazobenzene	120	225, 226	31.14
2-Acetylaminofluorene	181	180, 223	33.04
7,12-Dimethylbenz(a)anthracene	256	241, 239	36.97
2-Picoline	93	92, 78	7.70
Pentachloroethane	167	165, 119	12.00
Acetophenone	105	77, 51	14.19
N-Nitrosopyrrolidine	100	41, 42	14.24
N-Nitrosopiperidine	42	114, 55	15.16
Hexachloropropene	213	215, 211	17.12
1,4-Phenylenediamine	108	80, 81	18.19
Pentachlorobenzene	250	252, 248	22.94
1-Naphthylamine	143	144, 115	23.16
5-Nitro-o-toluidine	152	77, 106	24.22
Pentachloronitrobenzene	237	214, 295	26.82
N-Nitroquinoline-N-oxide	190	160, 89	29.60
3,3-Dimethylbenzidine	212	213, 211	33.69
Hexachlorophene	196	198, 209	39.26
N-Nitrosodiethylamine	74	42	9.88
o-Toluidine	106	107	14.05
Phentermine	58	91, 134	15.95
Sulfotep	97	322, 202	25.09
Aramite	135	193, 208	23.29
Phenacetin	108	109, 179	25.39

APPENDIX XI

Semivolatile Internal Standards With Corresponding Analytes Assigned For Quantitation

1,4-Dichlorobenzene-d4	Naphthalene-d8	Acenaphthene-d10
Phenol	Nitrobenzene	Hexachlorocyclopentadiene
Bis(2-Chloroethyl)ether	Isophorone	2,4,6-Trichlorophenol
2-Chlorophenol	2-Nitrophenol	2,4,5-Trichlorophenol
1,3-Dichlorobenzene	2,4-Dimethylphenol	2-Chloronaphthalene
1,4-Dichlorobenzene	Benzoic Acid	2-Nitroaniline
Benzyl Alcohol	bis(2-Chloroethoxy)methane	Dimethylphthalate
1,2-Dichlorobenzene	2,4-Dichlorophenol	Acenaphthylene
2-Methylphenol	1,2,4-Trichlorobenzene	2,6-Dinitrotoluene
Bis(2-chloroisopropyl)ether	Naphthalene	3-Nitroaniline
4-Methylphenol	4-Chloroaniline	Acenaphthene
N-Nitroso-di-n-propylamine	Hexachlorobutadiene	2,4-Dinitrophenol
Hexachloroethane	4-Chloro-3-methylphenol	4-Nitrophenol
Aniline	2-Methylnaphthalene	Dibenzofuran
Pyridine	Nitrobenzene-d5	2,4-Dinitrotoluene
Phenol-d5	2,6-Dichlorophenol	4-Nitroaniline
2-Chlorophenol-d4	Safrole	Fluorene
1,2-Dichlorobenzene-d4	Isosafrole, cis & trans	4-Chlorophenyl-phenylether
N-Nitrosodimethylamine	1,4-Naphthoquinone	Diethylphthalate
2-Fluorophenol	Butanamine, N-methyl-N-nitroso	1,2,4,5-Tetrachlorobenzene
Methanesulfonate methyl	Hexachloropropene	2,3,4,6-Tetrachlorophenol
Methanesulfonate ethyl	1,4-phenylenediamine	1,3-Dinitrobenzene
Phosphorothiotic acid	Phentermine	Thionazin
Ethanamine, N-methyl-N-nitroso		2,4-D methyl ester
N-Nitrosomorpholine		Diallate
2-Picoline		Phorate
Pentachloroethane		Dimethoate
Acetophenone		Silvex methyl ester
N-Nitrosopyrrolidine		2,4,5-T methyl ester
N-Nitrosopiperidine		2-Naphthaleneamine

1,4-Dichlorobenzene-d4	Naphthalene-d8	Acenaphthene-d10
N-Nitrosodiethylamine O-Toluidine		Pentachlorobenzene 1-Naphthylamine 5-Nitro-o-toluidine Pentachloronitrobenzene Sulfotep Aramite

Phenanthrene-d10	Chrysene-d12	Perylene-d12
4,6-Dinitro-2-methylphenol N-Nitrosodiphenylamine 4-Bromophenyl-phenylether Hexachlorobenzene Pentachlorophenol Phenanthrene Anthracene Carbazole Di-n-butylphthalate Fluoranthene 2,4,6-Tribromophenol 1,2-Diphenylhydrazine Dinoseb Pronamide Disulfoton Methyl parathion Ethyl parathion Isodrin Diphenylamine 1,3,5-Trinitrobenzene 4-Aminobiphenyl Methapyrilene, HCL N-Nitroquinoline-n-oxide 3,3-Dimethylbenzidine Phenacetin	Pyrene Butylbenzylphthalate 3,3'-Dichlorobenzidine Benzo(a)anthracene Chrysene bis(2-Ethylhexyl)phthalate Benzidine Terphenyl-d14 Chlorobenzilate Kepone Famphur P-Dimethylaminoazobenzene 2-Acetylaminofluorene 7,12- Dimethylbenz(a)anthracene Hexachlorophene	Di-n-octylphthalate Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene 3-Methylcholanthrene

APPENDIX XII

Comments On Analysis Of Appendix IX Semivolatile Compounds

Stock solutions of target Appendix IX compounds listed above were purchased from a commercial source (e.g. Supelco).

Appendix IX Semi-Volatile Mix 2	**# 4-6971**	**(A2)**
Appendix IX Semi-Volatile Mix 3	**# 4-6972**	**(A3)**
Appendix IX Semi-Volatile Mix 4	**# 4-6973**	**(A4)**
Appendix IX Semi-Volatile Mix 5	**# 4-6974**	**(A5)**
Appendix IX Semi-Volatile Mix 6	**# 4-7601**	**(A6)**

Some additional analytes required for analysis were not present in these available solutions. Therefore, a special certified custom mix was ordered from Supelco under lot # LA-69411 (A7). All purchased stock solutions contained all analytes of interest at a concentration of 2000 µg/mL each in methylene chloride.

Calibration standards were prepared in methylene chloride at five concentration levels (10, 25, 40, 60 and 80 ng/µL). Each calibration standard contains all compounds of interest, surrogates, and internal standards. The internal standards were added so that they were present in all calibration standards at a concentration of 20 ng/µL each.

Through preparation of mixed Appendix IX semivolatile standards, it has been documented that aramite, safrole, isosafrole, 3-methylcholanthrene , 3,3-dimethylbenzidine, methapyrilene HCL, hexachlorophene, and alpha,alpha-dimethylphenethylamine are unstable when combined in working solutions with other semivolatile target compounds, which limited expiration of the standard mixes to 3 months only.

Due to the nature of the Appendix IX compounds it was impossible to combine all six standard mixtures into one solution. Instead, Mixes #2 & #3 only were mixed together and the remaining standards were analyzed individually and resulted in good analytical resolution and easy identification of each components. Most of the analytes demonstrated excellent linearity, and their response factors were constant over the calibration range (%RSD <15). However, some analytes like kepone, 1,3,5-trinitrobenzene, 7,12-dimethylbenz(a) anthracene, 1,4-phenylenediamine, n-nitroquinoline-n-oxide, and hexachlorophene performed poorly due to the limited sensitivity and/or erratic chromatographic behavior.

Comments - Continued

Also it was discovered that n-nitrosodiphenylamine decomposes in the injection port and can not be separated with diphenylamine. Diastereoisomeric pair aramite and isosafrole can hardly be resolved on the RTX-5 column. Diallate and phorate as well as the pair of 2,4,5-T methyl ester and pronamide components are not resolved chromatographically and produce mass spectra containing ions contributed by both co-eluting analytes.

For Appendix IX and TCLP analyses, the compound 3-methylphenol (m-Cresol) coelutes with 4-methylphenol (p-Cresol). Since the spectrum and retention time for these two compounds are the same, these two compounds will be reported together as the sum of these two compounds and with the assumption that 3-methylphenol has the same response factor as the 4-methylphenol present in the standards.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8277

Determination of Polynuclear Aromatic Hydrocarbon Compounds by Selective Ion Monitoring (SIM) Method 8270C

Revision history:

Number	Date
0	02/05/98

UNCONTROLLED

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method is used for the determination of polynuclear aromatic hydrocarbon analytes in aqueous, soil, sediment, and other matrices by Selective Ion Monitoring (SIM) method. The SIM analysis scans for only a selected group of ions instead of a whole range of 35 to 500 m/z. The difference in scan time results in increased detector sensitivity, which allows us to report target analytes at very low levels.

1.1.2 This SOP follows SW-846 Method 8270C except for the specific deviations listed below or outlined in a project's specific QAPP.

1.1.3 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas/liquid/chromatography/mass spectroscopy and in the interpretation of chromatograms and mass spectra. Each analyst performing this method must have demonstrated the ability to perform the described chromatographic analysis and/or data interpretation.

1.2 Method Deviations & Comments

1.2.1 The following items represent deviations and comments of Method 8270C, as published, which are followed as standard operating procedure in the performance of this method at Laucks:

- Method 3611B (Alumina Column Cleanup and Separation of Petroleum Wastes) is utilized routinely for all soil/sediment sample extracts. Alumina cleanup is performed on aqueous sample extracts as deemed necessary.

- The 5 initial calibration levels have been established from 0.04ug/mL to 8.0ug/mL in order to demonstrate linearity for all target analytes and to provide a low-level standard that will act as the reporting limit as outlined in the method.

- Neutral surrogate compounds 1-Fluoronaphthalene, Fluorene-d10, and Pyrene-d10 are used routinely. Current surrogate recoveries are maintained in Laucks' quality control database (QC_DB).

- The concentration of internal standards added to all sample extracts and calibration standards has been decreased from 40 ng/uL per compound to 1.0 ng/uL in order to accommodate 2 µL injection volumes as allowed by the method.

- Acceptable retention times used for internal standards in all analyses is +/- 0.50 minutes relative to the daily CCV standard. This range is considerably narrower than the 0.06 RRT units specified in method 8270C and is considered more likely to ensure acceptable method performance.

- Laucks uses a relative response factor for all analytes. The method specifies that if the average RSD of all analytes for the initial calibration is ≤ 15%, then the RRF may be used for individual analytes with RSDs >15%. This method option will be used if any analyte's RSD exceeds 15% in the initial calibration.

- 8270 method DFTPP tuning criteria has been substituted as allowed by the method. Tuning criteria is listed in Appendix II.

- All standards are stored at -10°C or by the manufacturer's recommendation. Sample extracts are stored at 4°C.

- The surrogate and matrix spikes will be added to the sample such that the final amount injected from normally concentrated samples is 5 ng for all spiking analytes.

- For several ongoing projects Laucks uses relative response factors from the continuing calibration verification to quantitate the concentration in the sample. For future projects Laucks will use an average response factor from the initial calibration to calculate concentration from the sample.

1.3 Sample Collection, Sample Storage, Holding Times

1.3.1 Samples are normally collected in glass containers with Teflon-lined caps. All samples and sample extracts are stored at 4°C. Water samples must be extracted within 7 days of collection. Soil samples must be extracted within 14 days of collection. All sample extracts must be analyzed within 40 days of sample preparation.

1.4 Definition of Terms

1.4.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

Method Blank Spike	A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts or target analytes and surrogates are added each time sample extracts are prepared. Blank spikes are required on all HAZWRAP and NFESC work. In the context of this SOP, a blank spike is the same as a QC check standard.
CCC	Calibration Check Compound. A compound of analytical interest whose RRF in the CCV is compared to the average RRF from the initial calibration. The % difference must be less than the value specified in the method for the CCV to be considered valid. CCCs must also meet maximum %RSD criteria in an initial calibration.
CCV	Continuing calibration verification. This is the same acronym used in the CLP program. This is a standard injected at some prescribed frequency during the analysis sequence to determine whether the instrument has remained in calibration.
CLP	Contract Laboratory Program. The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In the context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.
DIW	Deionized water. Lab reagent water. Organic-free water. Since the systems used to provide DIW at Laucks all contain carbon polishing filters, they are capable of providing organic-free water for use in method blanks and method blank spikes.
IPCS	Instrument Performance Check Solution. A solution containing at a minimum DFTPP, pentachlorophenol, benzidine, and p,p'-DDT. The IPCS is analyzed at the start of a 12 hour QC period in order to verify DFTPP tuning criteria.
Internal Standard	A compound added to every standard, blank, matrix spike, matrix spike duplicate, and sample extract at a know concentration, prior to analysis. Internal standards are used as the basis for quantitation of target compounds.

MDL	Method detection limit. The lowest concentration in a sample which will yield a positive result that is greater than zero at a known level of confidence. MDLs are empirically determined by Laucks.
MDL Standard	Method detection limit standard. A standard prepared so that the concentrations of the target analytes are approximately 4x the empirically determined MDLs on an extract basis. This standard is used to verify that the instrument is capable of detecting the target analytes on an ongoing basis.
QC Period	Quality control period. An analysis sequence initiated by the injection of one or more standards, followed by sample extracts. A QC period is 12 hours starting with the injection of the CCV standard or DFTPP performance evaluation.
RF	Response Factor. The measure of the mass spectral response of an analyte compared to its internal standard. Response factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples. RF is determined by the following equation:

$$RF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

where:

A_x - Area of target analyte primary ion
C_{is} - Concentration of internal standard
A_{is} - Area of internal standard primary ion
C_x - Concentration of target analyte

RSD or %RSD	Relative standard deviation or percent relative standard deviation. The ratio of the standard deviation of a set of values to the mean of the set of values. A measure of the similarity of the values one to another.
RT	Retention time. The time (in minutes) at which a target analyte elutes from the GC column.

Sequence	A set of sample extracts and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.
SIM	Selective Ion Monitoring. This is a type of analysis when the MS detector is programmed to scan for only the selected ions.
Surrogate	Compounds added to every standard, blank, matrix spike, matrix spike duplicate, and sample extract at a known concentration; used to evaluate extraction and analytical efficiency by measuring recovery. Surrogates are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental samples.

2. Equipment List and Standards

2.1 Chromatographic System

Gas Chromatograph: Hewlett Packard 5890 I or II.

Carrier Gas: Helium 99.995% (high purity) or better.

Column: 30 m x 0.25 mm x 0.25 µf capillary column (Restek RTX-5 or equivalent).

Automatic Sampler: Hewlett Packard 7672A with 19405A and 3396A controllers.

GC/MS Interface: Capillary direct to the ion source of the mass spectrometer, fixed temperature.

Mass Spectrometer: Hewlett Packard 5970B.

Data System: Teknivent.

Miscellaneous: Assorted syringes, vials, caps, septa, injection port liners, ferrules, etc.

Note: All of the above equipment may be substituted with equivalent or better equipment.

2.2 Standards

2.2.1 Preparation of Semivolatile Standards

2.2.1.1 All standards prepared from this operating procedure must be logged into one of two standards preparation logbooks. One is maintained for stock solutions prepared from neat chemicals; the other is maintained for all working solutions. These logbooks are kept in the GC/MS semivolatile working area. When a standard is made, a solution number is assigned to it. This solution number is unique and will be used to track and identify the standard every time it is analyzed.

2.2.1.2 An example of the solution nomenclature used is a working PNA SIM standard prepared on 2/20/97. The solution number assigned was MS 5-70-04. This label represents the following:

MS	Solution was made and used as a Mass Spec standard.
5	Solution was logged into standard book #5.
70	Page number on which solution has been recorded.
4	This denotes the fourth entry on page 70.

2.2.1.3 All standards must also be verified both qualitatively and quantitatively in order to satisfy EPA requirements for traceability. This may be accomplished by purchasing solutions which have been fully documented by a commercial vendor.

2.2.2 Preparation of Internal Standard Solution (PNA SIM IS MIX @ 200 ug/mL).

Internal standards
Naphthalene-d8
Acenaphthene-d10
Phenanthrene-d10
Chrysene-d12
Perylene-d12
1,4-Dichlorobenzene-d4 (A)
(A) - this compound is present in the mix, but not appropriate to use for PNA analysis, and ,therefore, not reported)

2.2.2.1 Commercially prepared and certified internal standard solution is puchased at a concentration of 2000 µg/ml and is used as diluted 1:10 in methylene chloride. This standard is monitored for degradation by evaporative losses. The standard should be replaced when the area counts increase more than 15% from when it was freshly

opened. This standard is kept at -10°C until put into use. Once opened, the standard is kept at room temperature to avoid having the heavier compounds from falling out of solution.

2.2.3 Preparation of Surrogate Standards

Surrogate compounds
1-Fluoronaphthalene
Fluorene-d10
Pyrene-d10

2.2.3.1 Surrogate stock solutions are prepared by dissolving 100 mg of each analyte in 10 mL of methanol resulting in a stock solution with a concentration of 10,000 µg/mL.

2.2.3.2 0.5 mL of each of the PNA surrogate stock solutions are mixed and diluted in methanol to a final volume of 25 mL to make an intermediate working solution of 200 µg/mL. A 1.25 mL aliquot of the intermediate working solution is diluted in 25 mL of methanol to make a working solution of 5.0 ug/mL.

2.2.3.3 An aliquot of working solution is diluted 1:5 in methylene chloride and analyzed by the GC/MS department. The working solution must be within 80% - 120% of the expected values of 1 ng/µL for all three surrogates before they are put into use by the extractions department.

2.2.3.4 Commercially prepared and certified surrogate solution may be purchased and used in place of the above described solutions at the discretion of the laboratory.

2.2.4 Preparation of Matrix Spike Standards

Matrix Spike Compounds

Acenaphthylene	Chrysene
Acenaphthene	Benzo(b)fluoranthene
Fluorene	Benzo(k)fluoranthene
Phenanthrene	Indeno(1,2,3-cd)pyrene
Anthracene	Dibenzo(a,h)anthracene
Fluoranthene	Benzo(g,h,i)perylene
Pyrene	Benzo(a)anthracene
Benzo(a)pyrene	2-Methylnaphthalene

2.2.4.1 Commercially prepared and certified spiking solution SV Mix #5 is purchased from Restek. This standard solution containes all PNAs listed above at 2000 ug/mL in methanol with the exception of 2-methylnaphthalene. 2-Methylnaphthalene stock solution is prepared and verified in the same manner as surrogate standards.

2.2.4.2 625 uL of SV mix # 5 and 125 uL of 2-methylnaphthalene stock are mixed and diluted in 25 mL of methanol to prepare an intermediate working solution of 50 ug/mL. 2.5 mL of an intermediate working solution is diluted to a final volume of 25 mL in methanol to make a working standard solution of 5 ug/mL.

2.2.4.3 An aliquot of the working solution is diluted 1:5 in methylene chloride and analyzed by the GC/MS department. The working solution must be within 80% - 120% of the expected values of 1 ng/µL for all spiking analytes before they are put into use by the extractions department.

2.2.5 Preparation of DFTPP Solution

2.2.5.1 Prepare a solution of DFTPP (Decafluorotriphenylphosphine) at a concentration of 5000 µg/mL in acetone. Store this solution in amber screw-cap vials in the freezer. The vial in use may be stored at room temperature.

2.2.5.2 Commercially prepared and certified DFTPP solution may be purchased and used in place of the above described solution. This solution and working standards made from it are kept at -10°C.

2.2.6 Preparation of Calibration Standards

2.2.6.1 Calibration standards are prepared in methylene chloride from stock solutions which are purchased from a commercial source (e.g., Supelco or Restek). If an analyte required for calibration is not present in an available mixed solution, laboratory-prepared stock solutions which have been verified by GC/MS may be used. Laboratory prepared stock solutions should be tested against independent reference standards when they are available.

2.2.6.2 Calibration standards are prepared at six concentration levels (0.04, 0.4, 1.0, 4.0, and 8.0 ng/µL). Each calibration standard contains all compounds of interest, surrogates, and internal standards. The internal standards are added so that they are present in all calibration standards at a concentration of 2.0 ng/µL each.

2.2.7 Preparation of PNA200 stock solution

2.2.7.1 Assemble the following solutions in order to prepare a combined stock solution which will contain all analytes of interest at a concentration of 200 µg/mL each:

SV Calibration Mix 5 Restek #31011 (contains the following analytes at 2000 ug/mL)

Acenaphthylene	Chrysene
Acenaphthene	Benzo(b)fluoranthene
Fluorene	Benzo(k)fluoranthene
Phenanthrene	Indeno(1,2,3-cd)pyrene
Anthracene	Dibenzo(a,h)anthracene
Fluoranthene	Benzo(g,h,i)perylene
Pyrene	Benzo(a)anthracene
Benzo(a)pyrene	

2-Methylnaphthalene stock (10700 µg/mL) made from a neat (Chem Service)
Carbazol stock purchased from Supelco
Surrogate stock (made of individual standards. Each one was made from a neat.)

2.2.7.2 The vendor and catalog numbers provided are for reference only. Other vendor's certified solutions may be substituted.

2.2.7.3 Combine appropriate amounts of all solutions in a clean, silanized volumetric flask (2.0 or 5.0 mL capacity) so that all analytes are present at 200 µg/mL. Dilute to volume with methylene chloride, stopper the flask and mix well. Record all information in the working standards logbook and transfer the contents of the volumetric flask into silanized amber screw-cap vials. Store this solution in the freezer when not in use. The vial must be marked with the logbook name, standard type, preparation date, solvent used, and expiration date.

2.2.8 Preparation of working calibration standards

2.2.8.1 To prepare working calibration standards, add the amounts listed below (in µL) of PNA200 stock solution or PNA1.0 working solution, internal standard solution (PNA IS MIX @ 200 ug/mL) and methylene chloride to clean vial inserts and use within one week.

Preparation of Working Standards

	Amount Added Standard PNA200 (µl)	Amount IS Added (µl)	Amount CH_2Cl_2 Added (µl)
Working PNA 8.0	8	2	190
Working PNA 4.0	4	2	194
Working PNA 1.0	1	2	197

	Amount Added Standard PNA1.0 (µl)	Amount IS Added (µl)	Amount CH_2Cl_2 Added (µl)
Working PNA 0.4	80	2	118
Working PNA 0.04	8	2	190

2.2.8.2 Log into the working solutions logbook all of the above information as the standards are made. Store all standards at -10°C for up to one week when not in use.

2.2.8.3 The working PNA1 standard is made in larger quantity because it is used every day as a calibration check. It will be necessary to prepare a fresh PNA1 on a weekly basis.

2.2.8.4 Calibration stock solutions which are received sealed in ampules from the manufacturer are useable up to their manufacturer's expiration date. The mixed PNA200 stock solution is stable for up to 6 months or 1 year when promptly ampuled. Working calibration standards may be used for 1 week.

3. Safety precautions

3.1 Routine Safety Precautions

3.1.1 All standards and sample extracts should be handled as if they are hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.4 Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.5 Almost all of the analytes under consideration are known or suspected carcinogens. Analysts should wash their hands after using any standard, solvent or sample extract. Additionally, a respirator should be worn or a fume hood utilized for extremely hazardous compounds or very dirty extracts.

3.2 Waste disposal

3.2.1 All waste solvents, expired standards and old extracts should be disposed of in the solvent waste can located in the prep area fume hood. Consult the laboratory SOP for more detail on waste disposal.

4. Operation procedures

4.1 Analytical Conditions

4.1.1 Chromatographic Conditions

Initial Temperature:	80°C.
Initial Time:	2 minutes.
Column Temperature Program:	9°C/minute.
Final Temperature:	305°C.
Final Time:	8 minutes.
Injector Temperature:	250°C.
Transfer Line Temperature:	280°C.
Injector Purge Time Off:	42 seconds (0.7 minutes).
Injection Volume:	2 µL.
Column Linear Velocity:	30-40 cm/sec (nominal 35 cm/sec measured at 30°C).

4.1.2 Mass Spectrometer Conditions

Electron Energy:	70 volts.
Scan Time:	Not to exceed 1 second per scan.
Scan Start Time:	4.5 minutes.
Scan Time Range:	from 4.5 to 16.5 minutes.
Scans in Mass Segment:	125 to 177 amu.
Scan Time Range:	from 16.5 to 27 minutes.
Scans in Mass Segment:	165 to 245 amu.
Scan Time Range:	from 27 to 36 minutes.
Scans in Mass Segment:	248 to 280 amu.

4.2 Method Detection Limit Study

4.2.1 MDL studies will continue to be performed. This procedure is fully described in Laucks SOP on Determination of MDL's.

4.3 Method Reporting Limits

4.3.1 The method reporting limit for this method shall be set as described by method 8000B by using the lowest calibration standard as the method report limit. Values detected below this level will be reported but will be "J" flagged as outlined in Section 5.2 of this SOP.

4.4 Method Validation

4.4.1 Prior to the analysis of any samples, it is necessary to validate the method. A method validation study is performed in a similar manner to an MDL study with the exception that a minimum of 4 replicates are required and the concentration levels are typically higher. This procedure is fully described in Laucks SOP on Determination of Precision and Accuracy Studies.

4.5 Daily Instrument Maintenance

4.5.1 Daily instrument maintenance is required for good chromatography and proper calibration. The following steps must be undertaken as needed before the analysis of any standards or samples.

- Cool GC oven to 30°C.
- Check background.
- Remove injector septum and liner.
- Remove column from injector.
- Install a clean quartz liner.
- Reinstall O-ring or replace if worn.
- Install a new ferrule on the column.
- Clip off 8-10 cm of the column. Check for proper cut.
- Reinstall column in injector and adjust height.
- Install injector cap and a new septum.
- Clean and re-install the autosampler syringe.
- Check the background again.
- If background is okay, ramp the GC oven twice from 30°C to 300°C at 15°C/minute and hold 8 minutes.

4.6 Instrument Tuning

4.6.1 The HP 5970B mass spectrometer uses FC-43 (PFTBA) as a mass calibration compound. Each instrument will require different ion ratios to pass the required DFTPP performance criteria. See Appendix II for the DFTPP tuning criteria. The following ratios are therefore approximate. Use manual tuning to tune the mass spectrometer.

Ion	% of ion 69
69	100%
131	25-35%
219	25-35%
414	1-3%

4.6.2 Ion peak widths should be in the 0.5 to 0.6 amu range. Excessive peak width can lead to loss of minor isotope peaks. Insufficient peak width can result in the loss of sensitivity. Ions for water, nitrogen, and oxygen should be <5% of ion 69. A copy of the PFTBA spectrum and tabular listing should be kept with the instrument historical file.

4.7 Initial Multi-Point Calibration

4.7.1 An instrument performance check solution containing DFTPP should be injected first in order to verify DFTPP tuning criteria, degradation, and column tailing factors. The spectrum of DFTPP must pass tuning criteria before any other standards are injected. Retuning of the instrument may be necessary to achieve this. Additionally, the DFTPP spectrum should be well within the performance criteria - i.e., no ion abundance should be borderline and the ratios should be routinely reproducible to insure a stable calibration.

4.7.2 Analyze standard solutions using five different concentration levels. The lowest concentration should reflect the current report limit being used. The highest concentration should define the upper usable working range of the detector. Analyze the calibration standards following an acceptable DFTPP injection. The initial calibration must meet the criteria outlined later in this SOP.

4.8 Continuing Calibration Verification

4.8.1 At the beginning of a QC period, analyze an instrument performance check solution. The DFTPP tuning criteria in Appendix II must be met prior to analyzing a CCV standard. If DFTPP tuning criteria are met, analyze a CCV standard. The standard analysis must meet the %D and minimum RRF criteria detailed later in this SOP.

4.9 Sample Analysis

4.9.1 Analysis sequence

4.9.2 In general, the method blank accompanying the samples is injected prior to the analysis of the samples. This is not a requirement, however. Samples are then injected until the end of the 12 hour clock. After 12 hours have expired, instrument maintenance is performed and another IPCS and CCV standard are analyzed and evaluated before sample analysis continues.

4.9.3 Extract Preparation

4.9.4 Remove sample extracts from the refrigerator and allow them to come to room temperature.

4.9.5 Transfer 200 µL of extract to a vial insert.

4.9.6 Add 2 µL of IS solution (PNA IS MIX @ 200 ug/mL).

4.9.7 Cap the vial and mix well.

4.9.8 Place the vial onto the autosampler for analysis.

4.9.9 For dilutions, decide what dilution is necessary from previous data or analyst judgment. Make dilution and then add 2 µL of IS solution prior to capping vial. Mix well prior to analysis.

4.9.10 Compound Identification

4.9.10.1 Compounds are tentatively identified if a peak elutes within 0.5 minute of that compound in the CCV standard. In addition, the internal standard for that compound should also be within 0.5 minute of its counterpart in the CCV standard. To confirm the presence of that compound in the sample extract, the mass spectrum of the peak must be evaluated. Spectra are compared against standard spectra of each compound generated on the instrument used for analysis.

4.9.10.2 The following criteria are used to evaluate mass spectra:

- The intensities of the characteristic ions of a compound maximize within one scan of each other. Searches performed based on the presence of a target compound at a compound-specific retention time will be accepted as meeting this criterion.

- All ions present in the standard mass spectra at a relative intensity greater than 30% (most abundant ion in the spectrum equals 100%) or the three ions of greatest intensity must be present in the sample spectrum.

- The relative intensities of ions specified must agree within 30% between the standard and sample spectra. Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 20 and 80 percent.

- If a compound cannot be verified by all of these criteria, but in the technical judgment of the analyst, the identification is correct, then report that identification and proceed with quantification.

- The experienced analyst's judgment weighs heavily in evaluating chromatograms and mass spectra for compound identification. For instance, the retention times of surrogate compounds may be outside their expected windows due to sample matrix effects. If this has occurred, it must be fully documented in the appropriate report notes.

4.9.11 Common Analytical Problems

4.9.11.1 An analyst's professional judgment plays a large role in how data is interpreted. The following guidelines should be followed in order to facilitate consistency between analysts. Any anomalies not addressed in this SOP must be discussed with the supervisor prior to implementation. All anomalies and corrective actions must be documented.

4.9.12 Carryover

4.9.12.1 In some cases, if analytes in a sample are very high, there may be carryover from one analysis to the next. If a sample is suspected of being high due to historical data or extract color, the sample should be diluted prior to analysis, or one or more blanks should be analyzed after the sample to insure that there is no carryover between analyses.

4.9.12.2 However, in the case where high levels were not expected, and do appear in a sample analysis, the analysis after it should be examined carefully for carryover.

4.9.13 Manual Peak Integrations

4.9.13.1 Manual peak integrations should be used only when necessary to correct for matrix interference, tangent peaks, and rising baselines. Manual integrations are not to be used in an attempt to meet calibration, surrogate recovery, or spike recovery criteria.

4.9.13.2 If the chromatogram shows degradation due to sample loading e.g. split peaks, lift off, or severe tailing, the sample should be diluted and reanalyzed if required detection limits permit.

4.9.13.3 If a manual integration is necessary, follow the following guidelines:

- Integrate only the peak. Start where the peak lifts from the baseline and end as soon as it returns to the baseline. Do not integrate extra baseline in an attempt to increase peak area.
- Do not "peak shave". Do not cut off legitimate parts of the peak in order to reduce peak area.
- In cases of tangent skims, do not increase or decrease peak areas or heights by skimming extra long baselines or drawing the baseline too low.
- Always initial and date your manual integrations.

4.9.14 Compound Quantification

4.9.14.1 Aqueous samples

4.9.14.1.1 The equation for internal standard calculations is

$$Extract\ Concentration(ng/\mu L) = \frac{A_x \times C_{is}}{A_{is} \times RRF}$$

where:

A_x = Response for the target analyte
A_{is} = Response for the internal standard
C_{is} = Concentration of internal standard, in ng/µL
RRF = Relative Response Factor (calculated from the CCV)

4.9.14.1.2 The above equation is used directly by the HP computer to yield the extract concentration. To calculate the actual sample concentration, the following calculation must be used.

$$Sample\ Concentration(\mu g/L) = \frac{F \times D \times V_f \times GPC}{V_i}$$

where:

F = Amount found from HP quantitation report (ng/µL)
D = Dilution factor of extract
V_f = Final extract volume (µL)
GPC = GPC dilution factor. Use 1 if GPC was not performed, 2 if GPC was used
V_i = Initial sample volume (mL)

4.9.14.1.3 Normally, these calculations are automatically performed by the LIM system.

4.9.14.1.4 Any sample extracts which exceed the upper calibration range for any analyte of interest must be diluted and reanalyzed to bring the analyte into the working range of the calibration.

4.9.14.2 Non-aqueous samples

4.9.14.2.1 The results calculation for non-aqueous samples is very similar to that for aqueous samples. The only difference is the inclusion of a total solids term to calculate the dry weight equivalent of the initial sample size.

$$Sample\ Concentration(\mu g / L) = \frac{F \times D \times V_f \times GPC}{W_s \times T_s}$$

where:

W_s = Sample size extracted in grams.
T_s = Total Solids in decimal format (i.e. 0.76 not 76).

4.9.14.2.2 Any sample extracts which exceed the upper calibration range for any analyte of interest must be diluted and reanalyzed to bring the analyte into the working range of the calibration.

5. Reports

5.1 Data Packet Organization

5.1.1 See Appendix III for a check list detailing data packet organization.

5.2 Quality Control Reports

5.2.1 All results for quality control tests are entered into the lab data base. Printouts of all data entered must be included in the data packet. The routine minimum is a method blank report, a method blank spike report, and an MS/MSD report.

5.3 Sample Result Reports

5.3.1 Data Qualifying Flags

5.3.1.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

U: The analyte of interest was not detected, to the limit of detection indicated.

B: The analyte of interest was detected in the method blank associated with the sample, as well as in the sample itself. The B flag is applied without regard to the relative concentrations detected in the blank and sample.

J: The analyte of interest was detected below the practical quantitation limit. This value should be regarded as an estimate.

D: The value reported is derived from the analysis of a diluted sample or sample extract.

X: Indicates an unresolvable isomeric pair. This flag indicates that calculated results are the sum of the two isomers.

E: The value reported is based on a sample or sample extract in which the target analyte concentration exceeded the calibration range. The value reported should be considered an estimate.

6. Quality Control

6.1 General Issues

6.1.1 See Appendix VII and VIII for QA/QC limit and corrective action tables.

6.2 Initial Calibration

6.2.1 Criteria

6.2.1.1 Initial calibration data are evaluated using %RSD of the relative response factors as well as minimum average RRFs. The %RSD must be < 30% for each individual Calibration Check Compound (CCC). All other RRFs must be ≤ 15%. Alternatively, RRFs may be used as long as the average RRFs for all compounds in the method are ≤ 15% and the CCCs are < 30%.

6.2.1.2 Calculate the %RSD for all compounds. CCC criteria are listed in Appendix IV.

6.2.1.3 Calculate the individual and average RFs for each compound.

6.2.1.4 RFs are calculated using the equation

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Response of target analyte
A_{is} = Response of internal standard
C_s = Amount of target analyte (ng/µL)
C_{is} = Amount of internal standard (ng/µL)

6.2.1.5 The minimum acceptable average RF for all analytes is 0.050.

6.2.2 Corrective action

6.2.2.1 If the criteria are not met, other standards may be analyzed or appropriate instrument maintenance and analysis of new standards must be performed. Failure to achieve the required minimum average RRF for the SPCC compounds may indicate the need to perform instrument maintenance or prepare fresh calibration standards.

6.3 Continuing Calibration Verification

6.3.1 Criteria

6.3.1.1 At the beginning of each 12 hour QC period, a CCV standard is analyzed. The RF for each compound is calculated and the percent difference is calculated as follows:

$$\%Difference = \frac{RF_c - RF_i}{RF_i} \times 100$$

where:

RF_i = Average RF from Initial Calibration.
RF_c = RRF from CCV standard.

6.3.1.2 The %D results for all CCCs must be less than 20%. The %D for any other analytes should be < 30%.

6.3.1.3 In addition, all compounds must have a minimum RRF of at least 0.050. See Appendix V for all CCV criteria.

6.3.2 Corrective action

6.3.2.1 Check that all peaks have been properly integrated. Check the calculations. If the %D criteria are still not met, perform corrective instrument maintenance or re-tuning, and reanalyze the standard. If the %D or minimum RF criteria are still not met, a new CCV standard may need to be prepared, a new initial calibration performed, a new column installed, or other instrument maintenance performed in order to meet the CCV criteria.

6.4 Method Blank

6.4.1 Criteria

6.4.1.1 A method blank is used to verify contamination-free reagents and apparatus. A method blank is prepared with every set of samples extracted at the same time, at a frequency of at least one blank per 20 samples.

6.4.1.2 The concentration in a method blank of any analyte of concern should not be higher than the reporting limit. Any analyte response above the MDL is reported. Values below the reporting limit are "J" flagged. Method blank control limits are detailed in Appendix VI.

6.4.1.3 Where contractually required, e.g. Navy work, all analyte concentrations in the method blank must be <MDL.

6.4.2 Corrective action

6.4.2.1 The blank should be reanalyzed first if carry-over from a previously analyzed sample is believed to be the cause of the contamination. If the contamination is not present in the second analysis, the results of the second analysis may be used. Any similarly affected samples should also be reanalyzed.

6.4.2.2 If an analyte is found in the blank but not in any of the associated samples, the sample batch may not require re-extraction unless this is required by contractual obligations. Consult the QC officer to determine if re-extraction and reanalysis are required.

6.4.2.3 If any analyte exceeds the control limit in the blank and is also found in the associated sample extracts, the samples must be re-extracted and reanalyzed.

6.4.2.4 In any event, it is the laboratory's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the chromatograms be minimized. In the extreme case of chronic contamination, blanks may have to be analyzed from each stage of the sample processing to determine the contamination source so it can be eliminated. In all cases where blank contamination exceeds the control limit, a narrative comment must be made which documents the corrective actions taken.

6.5 QC Check Sample (LCS)

6.5.1 Criteria

6.5.1.1 The LCS is used to determine whether a method is in control during sample preparation and analysis. A LCS follows the same protocol as the matrix spike analysis except that the spiking solution is added to a blank matrix (deionized water for water or sea sand for soil/sediments) instead of an actual sample. Control limits are maintained in the Laucks quality control database (QC_DB)

6.5.2 Corrective action

6.5.2.1 Check all peak integrations and sample calculations.

6.5.2.2 If the analyte recoveries still exceed the control limits, the blank spike extract should be reanalyzed.

6.5.2.3 If the analyte recoveries are still out of control, re-extraction of the associated samples is required.

6.5.3 Matrix Spike

6.5.3.1 Criteria

6.5.3.2 A sample is chosen from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to extraction. It is not required that a matrix spike analysis be performed with each extraction batch unless the project QAPP requires it. However, the minimum frequency for MS analysis is 1 each per 20 samples per matrix. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of selected target analytes. Analyte recovery is calculated as follows:

$$\%Recovery = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Concentration in spiked sample.
SR = Native concentration in unspiked sample.
SA = Concentration of spike added.

6.5.3.3 The control limits for MS/MSD recoveries are available in the Laucks' quality control database (QC_DB).

6.5.4 Corrective action

6.5.4.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action may involve recalculation, re-extraction, and/or reanalysis. This process should also look at the recovery of surrogate compounds in the MS sample and at the recovery of matrix spiking compounds from the extraction batch blank spike analysis. In all cases, a narrative explanation of the condition is required to detail the corrective actions taken.

6.6 Matrix Spike Duplicate

6.6.1 Criteria

6.6.1.1 The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used to measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values.

6.6.1.2 This calculation is as follows:

$$RPD = \frac{S1 - S2}{(S1 + S2)/2} \times 100$$

where:

S1 = Measured concentration for MS sample.
S2 = Measured concentration for MSD sample.

6.6.1.3 The control limits for MS/MSD recoveries and RPDs are maintained in the Laucks quality control database (QC_DB).

6.6.2 Corrective action

6.6.2.1 Corrective action for RPD values which exceed the control limits follows the corrective action for MS/MSD recoveries. If more than one RPD exceeds the control limit, re-extraction may not be required if it can be demonstrated that the sample is non-homogeneous and all MS/MSD recoveries are within the control limits.

6.7 Surrogate Recovery

6.7.1 Criteria

6.7.1.1 Surrogates are chemically similar compounds added to every sample, method blank and QC sample prior to sample processing. They are used to monitor for potential sample processing errors and matrix effects. Surrogate compound recoveries are calculated as follow:

$$\%Recovery = \frac{S_m}{S_a} \times 100$$

where:

S_m = Concentration of surrogate measured in extract.
S_a = Concentration of surrogate added.

6.7.1.2 The control limits for surrogate recoveries recoveries are maintained in the Laucks quality control database (QC_DB).

6.7.2 Corrective Action

6.7.2.1 Check calculations for possible error.

6.7.2.2 Check instrument performance, if necessary correct the problem and re-analyze the extract.

6.7.2.3 Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant matrix interference. This may result in the dilution of the surrogate response to the point that the recoveries can not be measured. If the surrogate recoveries are available from a less-diluted or iundiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the QC limits, and no further action is required. For all package work both the diluted and undiluted analyses will be provided.

6.7.2.4 Re-extraction is not necessary in the case where a sample is chosen for MS/MSD analyses and the same recovery pattern is present in all three analyses. In this case, matrix effects may be assumed and re-extraction is not required for this sample.

6.7.2.5 All other circumstances require re-extraction and reanalysis of the affected sample(s).

6.7.2.6 Out of control surrogate recoveries in the method blank require that all the samples in the associated batch be re-extracted and reanalyzed. In any case, it is imperative to identify the problem associated with low recovery so that it can be corrected. It is a requirement that all out of control surrogate recoveries and the corrective action taken be discussed in the narrative.

7. References

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Method 8270C, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique," Revision 2, December 1996, U.S. EPA.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, 2nd Update, Method 3640A, "Gel-Permeation Cleanup," Revision 1, November 1992, US EPA.

US EPA. Contract Laboratory Program, Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, Document Number OLM03.1, August 1994.

APPENDIX I

Calibration Standard Solution Concentrations, ng/µL

Compound	STD1	STD2	STD3	STD4	STD5
1-Fluoronaphthalene	0.04	0.4	1.0	4.0	8.0
Naphthalene	0.04	0.4	1.0	4.0	8.0
2-Methylnaphthalene	0.04	0.4	1.0	4.0	8.0
Acenaphthylene	0.04	0.4	1.0	4.0	8.0
Acenaphthene	0.04	0.4	1.0	4.0	8.0
Fluorene-d10	0.04	0.4	1.0	4.0	8.0
Fluorene	0.04	0.4	1.0	4.0	8.0
Phenanthrene	0.04	0.4	1.0	4.0	8.0
Anthracene	0.04	0.4	1.0	4.0	8.0
Carbazole	0.04	0.4	1.0	4.0	8.0
Fluoranthene	0.04	0.4	1.0	4.0	8.0
Pyrene-d10	0.04	0.4	1.0	4.0	8.0
Pyrene	0.04	0.4	1.0	4.0	8.0
Benzo(a)anthracene	0.04	0.4	1.0	4.0	8.0
Chrysene	0.04	0.4	1.0	4.0	8.0
Benzo(b)fluoranthene	0.04	0.4	1.0	4.0	8.0
Benzo(k)fluoranthene	0.04	0.4	1.0	4.0	8.0
Benzo(a)pyrene	0.04	0.4	1.0	4.0	8.0
Ideno(1,2,3-cd)pyrene	0.04	0.4	1.0	4.0	8.0
Dibenz(a,h)anthracene	0.04	0.4	1.0	4.0	8.0
Benzo(g,h,i)perylene	0.04	0.4	1.0	4.0	8.0

APPENDIX II

DFTPP Tuning Criteria

Mass Relative Abundance

51	30-60% of mass 198
68	less than 2% of 69
69	present
70	less than 2% of 69
127	40-60% of mass 198
197	less than 1% of 198
198	100%
199	5-9% of mass 198
275	10-30% of mass 198
365	greater than 1.0% of mass 198
441	0-100 % of mass 443
442	40-100% of mass 198
443	17-23% of mass 442

8270 Method Criteria has been used as allowed by the method. The spectrum must be taken by averaging the peak apex with each of the adjacent scans and background subtracting not greater than 20 scans prior to the beginning of DFTPP.

APPENDIX III

Data Packet Check List

QC Summary
Surrogate Recovery Summary Report
Blank Spike Recovery Report
MS/MSD Recovery Report
Method Blank Summary
GC/MS Instrument Performance Check
Internal Standard Area and RT Summary Report

Sample Data
Target Compound Results (Organics Analysis Data Sheet)
Tentatively Identified Compound (TIC) Results (if required)
Sample Chromatograms, quantitation reports and spectra for all samples

Standards Data
Initial Calibration Summary Report
Chromatograms and quantitation reports for all initial calibration standards
Continuing Calibration Summary Reports
Chromatograms and quantitation reports for all CCV Standards

Raw QC Data
Bar Graph Spectrum, mass listing and chromatogram for every DFTPP injection
Method Blank Data
Target Compound Results (Organics Analysis Data Sheet)
Tentatively Identified Compound (TIC) Results (if required)
Chromatograms, quantitation reports and spectra for all method blanks
Blank Spike Data
Target Compound Results (Organics Analysis Data Sheet)
Chromatograms, quantitation reports and spectra for all blank spikes
Matrix Spike/Matrix Spike Duplicate Data
Target Compound Results (Organics Analysis Data Sheet)
Chromatograms, quantitation reports and spectra for all MS analyses
Control Charts

Bench Sheets
All extraction bench sheets, analysis log book pages, chains of custody, and any other pertinent information

APPENDIX IV

Initial Calibration Criteria

Calibration Check Compound	%RSD Limit
Acenaphthene	< 30%
Fluoranthene	< 30%
Benzo(a)pyrene	< 30%

RSD for all other analytes must be < 15%.

APPENDIX V

Continuing Calibration Verification Criteria

Calibration Check Compound	%D Limit
Acenaphthene	20%
Fluoranthene	20%
Benzo(a)pyrene	20%

%D for all other analytes must be within 30%.

APPENDIX VI

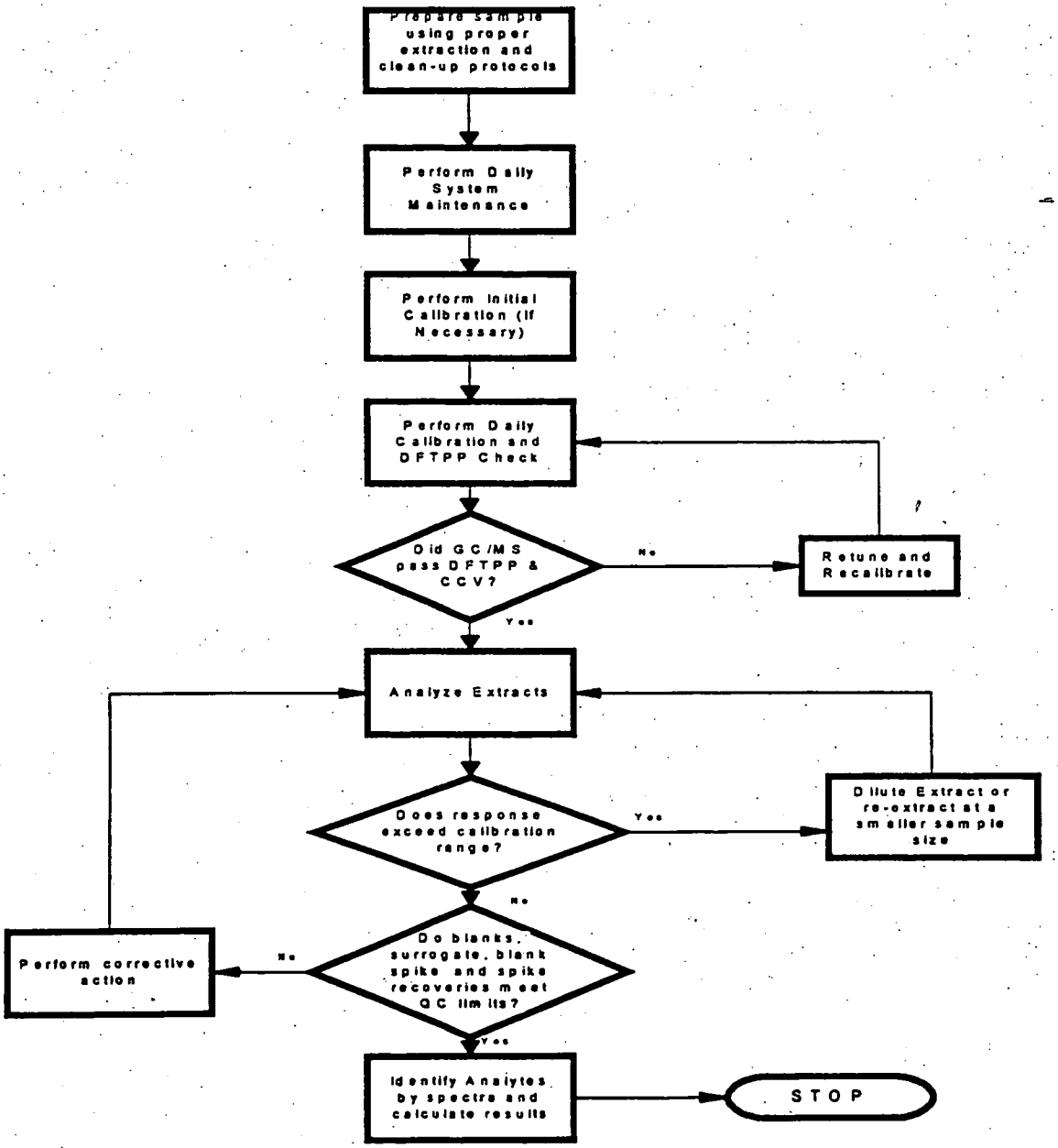
Method Blank Control Limits

Compound	Control Limits Water	Soil
All compounds	<RL	<RL

If contractually required, e.g. Navy work, all analyte concentrations must be < MDL in the method blank.

APPENDIX VII

Method 8270 Flow Chart



APPENDIX VIII

Method 8270C QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	Minimum of 5 levels, lowest near but above MDL, %RSD for CCC <30, All others should be <15%.	5 levels, %RSD for CCC <30, All others <15%, All RFs >0.05 Alternatively, average RSD must be <15%.	At minimum, yearly or as necessary due to major instrument maintenance or continuing difficulties meeting the CCV requirements.	Re-analysis of out of control standards.	Copies of all raw data, mass calibration, tune, and Form VI.
Internal Standards	Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12, all @ 40 ng/uL ea. Area must be -50% to +100% of the IS in the CCV. RT must be within ±0.06 RT units of the RT of the IS in the CCV.	Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12, all @ 2.0 ng/ul ea. Area must be -50% to + 100% of the area of the IS in the CCV. RT must be within 0.5 minutes of RT in CCV.	All standards, blanks, matrix spikes, matrix spike duplicates, blank spikes, SRMs, and sample re-extracts.	Re-analyze any sample which IS areas or RTs are out of range.	
DFTPP Tuning Verification (50 ng)	Mass Abundance 51 30-60% of 198 68 <2% of 69 69 present 70 <2% of 69 127 40-60% of 198 197 <1% of 198 198 100% 199 5-9% of 198 275 10-30% of 198 365 >1.0% of 198 441 present but < 443 442 40-100% of 198 443 17-23% of 442	Mass Abundance 51 30-60% of 198 68 <2% of 69 69 present 70 <2% of 69 127 40-60% of 198 197 <1% of 198 198 100% 199 5-9% of 198 275 10-30% of 198 365 >1.0% of 198 441 present but < 443 442 40-100% of 198 443 17-23% of 442	Every 12 hours; CLP Criteria is used as allowed by the method.	Retune instrument to pass criteria.	Copy of DFTPP check with the file.
Continuing Calibration Verification	Mid-level standard every 12 hours. %D <20% for CCCs, all others <30.	1.0 ng/ul standard every 12 hours. %D for CCC<20, all others<30.	Every 12 hours.	Perform system maintenance, re-analyze CCV standard.	Copies of raw data, mass calibration, tune, and Form VII.
Method Blank	Analytes must be <MDL	All analytes <RL.	One method blank per 20 samples or each extraction batch of samples, whichever is more frequent.	Re-analyze blank. If still out of control, re-extract the entire batch of samples unless the offending analyte(s) are not detected in the associated samples.	Notation in instrument log and case narrative if applicable.

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Surrogate Recovery	Upper and lower recovery limits determined by 3X standard deviation of at least twenty samples. To be performed at least semi-annually.	1-Fluoronaphthalene, Fluorene-d10, Pyrene-d10 surrogates are used. Limits are updated annually.	All samples, method blanks, blank spike, MS/MSD.	Re-extraction of the sample is required if any surrogate is out. All surrogates must be in control in the method blank otherwise all associated samples must be re-extracted..	Any out of control surrogates are to be documented in the instrument logbook and the job comments section or case narrative.
Blank Spike Recovery	Empirically derived from 20 or more BS. QC interval equals 3X standard deviation.	Empirically derived from 20 BS. QC interval equals 3X standard deviation.	One per batch of twenty.	Re-extract batch unless MS/MSD is perfect.	Narrate in case narrative.
MS/MSD Recovery & RPD	Empirically derived from 10 or more MS/MSD pairs. QC interval equals 3X standard deviation.	Empirically derived from 10 or more MS/MSD pairs. QC interval equals 3X standard deviation.	One per batch of twenty.	Re-extract batch unless blanks spike is perfect or documentable matrix effect is present.	Narrate problems in case narrative.

APPENDIX IX

Analytes Ammenable to Analysis by Method 8270C SIM

Current 8270 SIM PNA Target Analytes:

Compound	Primary Ion	Secondary Ion(s)
Naphthalene	128	129,127
2-Methylnaphthalene	142	141
Acenaphthylene	152	151,153
Acenaphthene	153	154,152
Fluorene	166	165,167
Phenanthrene	178	179,176
Anthracene	178	176,179
Carbazole	167	166
Fluoranthene	202	200
Pyrene	202	200,203
Benzo(a)anthracene	228	229,226
Chrysene	228	226,229
Benzo(b)fluoranthene	252	253
Benzo(k)fluoranthene	252	253
Benzo(a)pyrene	252	253
Indeno(1,2,3-cd)pyrene	276	274
Dibenzo(a,h)anthracene	278	279
Benzo(g,h,i)perylene	276	274,277
1-Fluoronaphthalene	146	147,145
Fluorene-d10	176	174,177
Pyrene-d10	212	

APPENDIX X

Elution Order of the Compounds

Compound	Retention Time (min)
Naphthalene	8.71
2-Methylnaphthalene	10.57
Acenaphthylene	13.09
Acenaphthene	13.62
Fluorene	15.04
Phenanthrene	17.76
Anthracene	17.89
Carbazole	18.41
Fluoranthene	21.16
Pyrene	21.78
Benzo(a)anthracene	25.19
Chrysene	25.31
Benzo(b)fluoranthene	28.13
Benzo(k)fluoranthene	28.21
Benzo(a)pyrene	29.08
Indeno(1,2,3-cd)pyrene	33.00
Dibenzo(a,h)anthracene	33.06
Benzo(g,h,i)perylene	34.11
1-Fluoronaphthalene	8.70
Fluorene-d10	14.96
Pyrene-d10	21.74

APPENDIX XI

Semivolatile Internal Standards With Corresponding Analytes Assigned For Quantitation

Naphthalene-d8	**Acenaphthene-d10**
Naphthalene	Acenaphthylene
2-Methylnaphthalene	Acenaphthene
1-Fluoronaphthalene	Fluorene
	Fluorene-d10

Phenanthrene-d10	**Chrysene-d12**	**Perylene-d12**
Phenanthrene	Pyrene	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
Carbazole	Chrysene	Benzo(a)pyrene
Fluoranthene	Pyrene-d10	Indeno(1,2,3-cd)pyrene
		Dibenzo(a,h)anthracene
		Benzo(g,h,i)perylene

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-8302

Title: HPLC Ordnance Data Review

Revision history:

Number	Date
0	07/31/95
1	01/23/98

Revised by: _____ Date: 1/30/98
Monica Carr, Organic Division Manager

Approved by: _____ Date: 1-30-98
Harry Romberg, QC Officer

Approved by: _____ Date: 1/26/98
Karen Kotz, Laboratory Director

UNCONTROLLED

Summary

The data reviewer will be working on reviewing data packages which have been completed by the HPLC analyst. The review will follow this procedure, utilizing reference materials attached to this procedure as well as client/project specific requirements (such as Maximum % RSD and CRDLs, if different from EPA PQLs), which will be provided by the HPLC Supervisor. All data review will be documented on the "Data Review Checklist" (attached to this procedure) and comments will be referenced to the Review Item and number. At the end of the review process, the reviewer will arrange the data package in the order specified here, with the completed "Data Review Checklist" and accompanying notes from the analyst(s) (if applicable) on the top of the package. This package will be given to the HPLC Supervisor for final review and narrative preparation.

List of Attachments

1. Laucks Testing Labs - Data Review Checklist [DRC] (HPLC - Ordnance Version)

Procedure

1. Initial Information

   A. Before beginning the review process, it is important to confirm with the HPLC Supervisor what method was used and what the associated QC limits are. Most of this information is printed on the following forms, however it must be confirmed that these QC limits are correct for the method/client/project. The levels for the following QC criteria should be confirmed:

Initial Calibrations:	Maximum %RSD	*(usually 20%, will be on Form V)*
Continuing Cals:	Maximum %D	*(usually 15%, will be on Form VII & ICV)*
Surrogates:	Acceptable Recovery Range *(will be on Form II)* and spiking levels *[100 ul of Surrogate Spike Soln. Residue levels for Water and Soil will be 2 ppm.]*	
Blank:	Maximum Allowable Concentration for confirmed compounds	
MS/MSD:	QC Limits for % Rec and % RPD *(on Form III)* and spiking levels *[100 ul of Spiking Solution. Water will be 4 ppb, Soil will be 133 ppb.]*	

   B.

Laucks forms in the data package	Laucks #	*EPA Equivalent*
QC Summary Data:		
"Surrogate Recovery Summary Report"	SURR GC	*Form II*
"MS/MSD Report" *and Blank Spikes/Duplicates*	BLKSPK-1 BLKSPK-2 MS/MSD-1 MS/MSD-2	*Form III*
"Method Blank Summary"	BLK SUMM	*Form IV*
Sample Data: *(and Raw QC Data)*		
"Organics Analysis Data Sheet"		*Form I*
"Compound Confirmation"	GC CONF	*Form X*

B. Laucks forms in the data package *(continued)*

	Laucks #	*EPA Equivalent*
Standards Data:		
"Initial Multi-point Calibration"	ICAL GC	*Form VI*
Cal. Factors:	Part 1	
RTs:	Part 2	
Peak Response (Areas):	Part 3	
Linear Regression:	Part 4	
"Initial Calibration Verification Worksheet"	ICV-1	
"Continuing Calibration Verification Worksheet"	CCV-1	*Form VII*
Calibration Factor:	Page 1	
Retention Times:	Page 2	

2. Overall Review

   A. Review Narrative already written by analyst to familiarize yourself with the project and to confirm what comments have already been written.

<u>QC Summary</u>

3. Form II ("Surrogate Recovery Summary Report")

   A. Confirm all sample and QC are present by comparing to the bench sheet.
   Check "Yes" or "No" on DRC #A1. Discrepancies must be noted on the DRC, referencing #A1.

   B. Check to make sure the recoveries for surrogates are within QC limits. Outliers will be marked with an "*". Comment on any that are outside limits or are not present (have been diluted out).
   Check "Yes" or "No" on DRC #A2 at completion of review. If any recoveries are outside QC Limits, these must be noted on the DRC, referencing #A2.

4. Form III ("MS/MSD Report" *and Blank Spikes/Duplicates* BLKSPK-1,2, MS/MSD-1,2)

   A. **BLKSPK-1 and/or MS/MSD-1** - Confirm the spike added against the normal levels of 4 ppb for water, 133 ppb for soil. If not the normal levels, confirm against the bench sheets and log books.

   B. **BLKSPK-1 and/or MS/MSD-1** - Check the amount found against Form I's (these are entered manually on Form III's) for the corresponding sample (check Lab ID against bench sheet). Check to see if any % Rec, and/or RPD's are out of control (will be indicated with an "*").
   Check "Yes" or "No" on DRC #A3 and #A4 at completion of review. The number and type (high or low) of out of controls must be noted on the DRC, referencing #A3 and/or #A4 followed by the Lab ID # where the out of controls occurred.

   C. **BLKSPK-2 and/or MS/MSD-2** - Check that the correct samples are associated with the blank spike and/or MS/MSD by confirming against the bench sheet.
   Check "Yes" or "No" on DRC #A5 at completion of review. Discrepancies must be noted on the DRC, referencing #A5.

5. Form IV ("Method Blank Summary")

   A. Check the blank name and corresponding lab ID numbers against the bench sheet.
   Check of "Yes" or "No" on DRC #A6. Discrepancies must be noted on the DRC, referencing #A6.

Standards Data

7. Form VI ("Initial Multi-point Calibration" ICAL HPLC

Cal. Factors:	Part 1
RTs:	Part 4
Peak Response (Areas):	Part 2
Linear Regression:	Part 3
Amount Summary:	Part 5

   A. **Part 1** - Check that % RSD is within 20% limits (will be marked with a "*" if outside limit). Also confirm that the lab file ID's match those on the Target Sequence for the ICAL.
   Check "Yes" or "No" on DRC #C2 at completion of review. Discrepancies must be noted on the DRC, referencing #C2.

8. "Initial Calibration Verification Worksheet" ICV-1

   A. There may be an ICV Form for the mid-point standard from the ICAL, but only if samples were analyzed directly after the ICAL, before another CCV. Check that there is an ICV associated with each analytical batch of samples reported here by checking date and time against Form IV ("Method Blank Summary"). If unclear as to which ICVs correspond to the samples, the Target Sequence should be referenced.
   Check "Yes" or "No" on DRC #C1 at completion of review. Discrepancies must be noted on the DRC, referencing #C1.

   B. Confirm that %D's are within limits (15%). They will be marked with a "*" if out.
   Discrepancies must be noted on the DRC, referencing #C1.

9. Form VII ("Continuing Calibration Verification Worksheet" CCV-1)

Calibration Factor:	Page 1
Retention Times:	Page 2

   A. **Page 1** - Check that % D is within 15% control limits. Confirm that all forms are included here by comparing against the Target Sequence.

   B. **Page 2** - Confirm Continuing Calibration RTs are within RT window (note: these will **not** be marked with a "*" if out of control).

   Check "Yes" or "No" on DRC #C4 at completion CCV of review. Discrepancies must be noted on the DRC, referencing #C4.

10. Chromatograms and Processed Files
   A. Confirm that chromatograms and processed files for all calibration standards and CCVs are present.
   Check "Yes" or "No" on DRC #C5 at the completion of review. Discrepancies must be noted on the DRC, referencing #C5.

Sample Data and Raw QC Data

12. Form I ("Organics Analysis Data Sheet")

A. Check dates received and dates of collection against the SDG Database Report, and date extracted against the extraction bench sheets. Confirm that the dates extracted and analyzed were within holding times.
Extraction: 14 days for soils and 7 days for waters (measured from date of collection).
Analysis: 40 days from extraction.
Check "Yes" or "No" on DRC #B1 at the completion of review. Discrepancies must be noted on the DRC, referencing #B1.

B. Check sample size against the bench sheet - the initial sample (there are sometimes many dilutions) will always be a 1:2 dilution for water and soil. Confirm that the percent moisture is correct by comparing to the SDG report (for soils). Waters should always be 100% moisture.
Check "Yes" or "No" on DRC #B2 at the completion of review. Discrepancies must be noted on the DRC, referencing #B2.

C. Check that all "hits" are correctly transferred to Form I from Form X (unless they are crossed out on Form X). In addition, check the retention times of the analyte to ensure that they are within the RT window. The retention times and RT windows are located on the compound confirmation sheet.
Check "Yes" or "No" on DRC #B3 at the completion of review. Discrepancies must be noted on the DRC, referencing #B3.

D. Were all samples with analyte concentrations > the highest calibration standard diluted and reanalyzed? If so, were the diluted sample results linear with the last result that exceeded calibration (i.e. within 25%)?
Check "Yes", "No" or "N/A" on DRC #B4 at completion of review. Discrepancies must be noted on the DRC, referencing #B4.

E. Check that the sample number on Form I matches that on the chromatogram.
Check "Yes" or "No" on DRC #B5 at the completion of review. Discrepancies must be noted on the DRC, referencing #B5.

F. Check that flags are used correctly. Flags not referenced on the "Use of Data Qualifiers" Memo are detailed below.
"D" These flags are used on diluted sample results, but are not used on the initial 1:2 dilution as this is a dilution of methanol with water to produce the appropriate sample matrix for HPLC analysis.
"E" Anything above 1000 ppb extract concentration on Form X must be flagged with an "E" on Form I and re-diluted to attain an accurate analysis within the calibration curve.
"X" This will be used for the most accurate "hit" from all the dilutions. Only one "X" for each sample/analyte should occur throughout the dilutions, as there is only one "most accurate" hit.
"Z" A "Z" flag on sample report forms indicates coelution has occurred between two or more target analytes on the confirmation CN column. For this reason, quantitative confirmation is not possible.
Discrepancies must be noted on the DRC, referencing #B6.

13. Form X ("Compound Confirmation")

    A. Check that any %D over 25% is "P" flagged on Form I (note that blank and matrix spikes are not confirmed and %D's reported should be crossed out for blank spikes).
    Check "Yes" or "No" on DRC #B6 at the completion of review of data qualifiers. Discrepancies must be noted on the DRC, referencing #B6.

    B Check the retention time windows located on the the compound confirmation form, with the copy of the retention time window study located in the Bench Sheet section of the data package.
    Check "Yes" or "No" on DRC #B7 at the completion of review of data qualifiers. Discrepancies must be noted on the DRC, referencing #B7.

At the end of the Sample Data and Raw QC review, remove all Form Xs and place them at the end of the Standards Data set.

14. Final Review
    A. Were recoveries for the SRM (if required by client/project) within QC Limits?
    Check "Yes", "No" or "N/A" on DRC #D2 at completion of review. Discrepancies must be noted on the DRC, referencing #D2.

    B. Are all nonconformances included and noted on the DRC?
    Check "Yes" or "No" on DRC #D1 at completion of review. Discrepancies must be noted on the DRC, referencing #D1.

17. Order of Final Packet - All in numerical and chronological order and in order by column
    Check "Yes" or "No" on DRC #D3 at review completion. Note discrepancies referencing #D3.

    1. QC Summary
       Forms II through IV

    2. Sample Data
       For each sample, the following packet:
       All Form I's, then chromatograms and integration reports *(C18 first, then CN column)*

    3. Standard Data
       Form VI's (Parts 1,2,3, and 4) *(C18 column first, then CN column on each)*
       ICV-1 (Initial Calibration Verification Sheets)
       Form VII's (Pages 1 and 2) *(C18 column first, then CN column on each)*
       Form X's *(samples first, followed by QC samples)*
       Raw Standards Data, *(compound confirmation, chromatograms and integration reports)*
       including:
       Multi-point calibrations *(C18 column, then CN column)*
       All CCVs and ICVs in chronological order
       MDL Standard
       I Blanks

4. Raw QC Data *(Method Blanks, Blank Spikes/Blank Spike Duplcts, MS/MSDs, Control charts.)*
   For each sample, the following packet:
   All Form I's, then chromatograms and integration reports *(C18 first, then CN column)*

5. Bench Sheets
   Including: SDG Report, Copy of instrument logbook, Extraction bench sheets, Logbooks for surrogates/spikes (referenced on bench sheet), Logbooks for standards, RT Study.

Attachment 1
Data Review Checklist

Laucks Testing Labs Data Review Checklist
Ordnance 8330 - HPLC Department

Work Order Number:	
Analysis Batch Dates:	
Method:	SDG #:

Review Item	Yes	No	N/A	2nd Review
A. QC Summary 1. Are all required QC results present?				
2. Do surrogate recoveries meet QC limits?				
3. Are blank spike/blank spike duplicate results correct and do they meet QC %Rec and RPD limits?				
4. Are MS/MSD results correct and do they meet QC %Recovery & RPD limits?				
5. Are correct samples associated with the blank spike(s) and/or MS/MSDs?				
6. Are all blanks reported?				
7. Is MDL recovery within QC limits?				
B. Sample Data and Raw QC Data 1. Were samples extracted and analyzed within holding times?				
2. Are sample sizes and % moisture correct?				
3. Are all hits recorded correctly?				
4. Were samples diluted as required and were dilutions linear (within 25% of last value)?				
5. Were sample ID's checked?				
6. Were data qualifier flags used correctly?				
7. Were the retention time windows on the compound confirmation form recorded properly? Review RT study located in Bench Sheet section.				
C. Standards Data 1. Is there an ICV run every day and are all %Ds within QC limits?				
2. Are calibration %RSDs within QC limits?				
3. Are all ICVs and CCVs recorded and are RT %Ds within QC control limits?				
4. Are CCV %Ds and RTs within QC limits?				
5. Is all raw data present?				
D. Final Review 1. Are all nonconformances listed?				
2. Are recoveries for the SRM within limits?				
3. Are all components of the data package present and in correct order?				

Laucks Testing Labs Data Review Checklist
Ordnance 8330 - HPLC Department

Work Order Number:	
Analysis Batch Dates:	
Method:	SDG #:

Comments on any "No" responses:

_____
_____
_____
_____
_____
_____
_____
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_____
_____
_____
_____
_____

Data Reviewer: _____ **Date:** _____

2nd Level Reviewer: _____ **Date:** _____

LAUCKS TESTING LABORATORIES INC.

Seattle, Washington

SOP #:LTL-8330

Determination of Nitroaromatics and Nitramines by SW-846 Method 8330A

Revision history:

Number	Date
1	06/19/95
2	01/11/96
3	04/10/96
4	04/15/96
5	07/09/96
6	12/18/97
7	4/30/98
8	10/28/98
9	01/25/99
10	03/16/00

Controlled Document

No. 20 Assigned to: Tetra

Revised by: Monica Carr — Date: 3/22/00
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Approved by: Harry Romberg — Date: 3-22-2000
Harry Romberg, QA Officer

Approved by: Kathy Kreps — Date: 03-23-2000
Kathy Kreps, Laboratory Director

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method is used for the trace analysis of ordnance compounds in water, soil, and sediment samples by high performance liquid chromatography. The concentrated water sample extracts are diluted 1:1 (v/v) with reagent grade water prior to analysis. The sample extracts are analyzed using a C18 (octadecyl) reverse phase column, and target analyte concentrations are measured at either 254 nm or 210 nm using a UV detector. All positive measurements observed on the C18 column are confirmed by a second analysis which uses a CN (cyano) column and C8 column in series. The C18 column is considered the primary column and is used for quantitation of all target analytes.

1.1.2 This method is used to determine part per billion levels of the ordnance analytes listed below:

Compound	Acronym
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX
1,3,5-Trinitrobenzene	1,3,5-TNB
1,3-Dinitrobenzene	1,3-DNB
Methyl-2,4,6-trinitrophenylnitramine	Tetryl
Nitrobenzene	NB
2,4,6-Trinitrotoluene	2,4,6-TNT
4-Amino-2,6-dinitrotoluene	4-Am-DNT
2-Amino-4,6-dinitrotoluene	2-Am-DNT
2,4-Dinitrotoluene	2,4-DNT
2,6-Dinitrotoluene	2,6-DNT
2-Nitrotoluene	2-NT
3-Nitrotoluene	3-NT
4-Nitrotoluene	4-NT

6 Additional Compounds
(Separate Analysis at 254 nm)

Compound	Acronym
2,4-Diamino-6-nitrotoluene	2,4-DA-6-NT
2,6-Diamino-4-nitrotoluene	2,6-DA-4-NT
3,5-Dinitroaniline	3,5-DNA
1-Nitroso-3,5-dinitro-1,3,5-hexahydrotriazine	MNX
1,3,5-Trinitroso-1,3,5-hexahydrotriazine	TNX
2,2',6,6'-Tetranitro-4,4'-azoxytoluene	4,4'-TN-AZOXY

PETN/NG Compounds
(Separate Analysis at 210 nm)

Compound	Acronym
Nitroglycerin	NG
Pentaerythritoltetranitrate	PETN

1.1.3 Aqueous samples of higher concentration can be directly analyzed by diluting 1:1 (v/v) with methanol or acetonitrile, filtering, separating on a C18 reverse phase column, and determined at either 254 nm or 210 nm, and confirmed on a CN column.

1.1.4 This method is restricted to use by, or under the supervision of, analysts experienced in the use of high pressure liquid chromatography and in the interpretation of chromatograms. Each analyst performing this method must have demonstrated the ability to perform the described chromatographic analysis and/or data interpretation.

1.2 Method Deviations & Comments

1.2.1 The following items represent deviations from the published version of method SW 8330 which are followed as standard operating procedure in the performance of this method at Laucks.

1. Single injections of calibration standards are analyzed rather than triplicate injections in a random order. It has been determined at Laucks that single injections of these standards yield acceptable calibration and linearity data as evidenced by the calculated percent RSDs used to evaluate the initial calibration data.

2. Method SW 8330 specifies that all analyses are to be performed using a mobile phase which consists of a 50:50 mixture of methanol/water under

isocratic conditions. Laucks employs a gradient elution program (detailed in Section IV) in order to improve the separation of the target analytes on the CN-C8 column.

3. According to Method 8330, all working standards are to be prepared daily in a methanol/calcium chloride solution. The practice at Laucks for 8330 and the 6 additional compounds is to prepare working standards using acetonitrile and diluting 50/50 with water just prior to analysis. NG/PETN are prepared in a 50/50 mixture of acetonitrile and water. These working solutions have been demonstrated to be stable for at least 6 months. The stability of target analyte responses in the working solutions in use (especially that of tetryl) is used to determine whether new solutions should be prepared.

4. Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. Laucks has experienced erratic recovery of tetryl from spiked sample extracts.

5. Currently, the confirmation column can demonstrate full separation for the ordnance compounds. However, from time to time, the following target analyte pairs will partially co-elute: 4-Amino-2,6-dinitrotoluene and tetryl. Therefore, positive confirmation can not be made when these two peaks have been tentatively identified on the primary column.

6. At the time of this writing, analysis of the 6 additional compounds (not including PETN/NG) combined with the 14 ordnance compounds results in the separation of all compounds on the primary column (C18).

7. Although the compounds NG and PETN are not listed in SW 846 Method 8330, Laucks has found that adequate recovery of these compounds can be achieved using this method by modifying the wavelength from 254 nm to 210 nm.

8. Picric and picramic acids exhibit substantial peak shift and may elute near or co-elute with HMX on the C18 column using the 8330 method. However, no attenuation compounds, nor NG/PETN coleute on the primary (PAH) column using the picric/picramic method. The buffer is used in this method in order to stablize these compounds.

1.2.2 In order to attain lab-wide consistency among staff members for decision-making processes with regard to laboratory anomalies, several common items have been addressed in this SOP. Any occurrences which are not covered in this SOP should be discussed with the supervisor, prior to implementing a solution.

1.2.3 One example is the determination of potential carry-over in sample analyses. Any samples analyzed subsequent to a high level sample (which is defined by yielding one or more target analytes above the calibration range) should be thoroughly examined for potential carry-over of the same target analyte(s). Corrective action in the form of reanalysis for possible carry-over should be performed and documented in the narrative.

1.2.4 Another example is the review of all sample chromatograms for analytes which may not show up on the sample quantitation report due to data system error or retention time shift. All peaks should be examined and evaluated based on the retention times and sample concentration in order to prevent reporting false negatives.

1.3 Sample Collection, Sample Storage, Holding Times

1.3.1 Samples are collected in amber glass containers with Teflon-lined caps. All samples and sample extracts are stored at 4°C ±2°C. According to guidelines listed in SW-846 for the extraction of semivolatile compounds, water samples must be extracted within 7 days of collection, and soil samples must be extracted within 14 days of collection. All extracts must be analyzed within 40 days of sample preparation.

1.3.2 Although not a routine sampling practice, a soil holding time study performed by the U.S. Army Cold Regions Research and Engineering Laboratory recommends a maximum holding time of eight weeks when samples are frozen.

1.3.3 A similar study performed for water samples recommends a maximum holding time of 50 days for relatively sterile samples which are refrigerated. Surface waters, or samples likely to have significant microbial activity, may suffer significant losses of nitroaromatic compounds (particularly trinitrobenzene and trinitrotoluene) within 1-2 days, even under refrigeration. If microbial activity is suspected, water samples should be extracted as soon after collection as is practical.

1.4 Definition of Terms

1.4.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

Method Blank Spike	A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts of target analytes and surrogates are added each time sample extracts are prepared. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard.

CCV	Continuing calibration verification. This is the same acronym used in the CLP program. This is a standard injected at some prescribed frequency during the analysis sequence to determine whether the instrument has remained in calibration.
CF	Calibration factor. The ratio of peak response to nanograms injected. This term is defined in the same way in both the CLP contract and SW-846.
DIW	Deionized water. Lab reagent water. Organic-free water. Since the systems used to provide DIW at Laucks all contain carbon polishing filters, they are capable of providing organic-free water for use in method blanks and method blank spikes.
IBLK	An instrument blank is solvent containing the method surrogates and is injected into the instrument to monitor for carryover between sample extract injections.
ICV	Initial calibration verification. It is a standard which is injected at the start of each QC period that is compared to the initial multi-point calibration to determine whether the instrument is still in calibration.
IDL	Instrument detection limit. The lowest concentration of a target analyte that will yield a signal:noise ratio of at least 3x. Used as a starting point for selecting MDL study spiking levels.
MDL	Method detection limit. The lowest concentration in a sample which will yield a positive result that is greater than zero at a known level of confidence. MDLs are empirically determined at Laucks.
QC Check Standard	Quality control check standard. Referred to in this SOP as a blank spike. A QC check standard is a requirement of SW-846 method 8000 and is used to determine whether the analytical system is in control if MS/MSD recoveries are out of control. See also blank spike.

QC Period	Quality control period. An analysis sequence initiated by the injection of one or more standards, followed by sample extracts, and terminated with a standard injection. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP.
Reporting Limit	Also known as PQL, or Practical Quantitation Limit. This is determined the by low level standard concentration.
RSD or %RSD	Relative standard deviation or percent relative standard deviation. The ratio of the standard deviation of a set of values to the mean of the set of values. A measure of the similarity of the values one to another.
RT	Retention time. The time (in minutes) at which a target analyte elutes from the LC column.
RT Window	Retention time window. The ± value which is applied to the ICV to establish the time range used to make tentative compound identifications.
Sequence	A set of sample extracts and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.

2. Equipment List and Standards

2.1 Chromatographic System

Primary Column:	C18 (octadecyl) reverse phase HPLC column, 15 cm x 4.6 mm, 5 µm particle size, (Rainin Microsorb or equivalent).
Secondary Column:	CN (cyano) reverse phase HPLC column, 25 cm x 4.6 mm, 5 µm particle size, (Supelcosil LC-CN or equivalent).
	C8 and CN reverse phase HPLC columns in series, 10cm x 3.9mm, 4µm particle size, (Waters Nova- Pak or equivalent). These are used in the for the analysis of the 6 additional compounds.

Mobile Phase:	Methanol (EM Science brand high purity solvent or equivalent). Reagent water (Modulab Polisher HPLC grade water or equivalent).
UV Detector:	254 nm (210 nm for NG and PETN)
HPLC System:	Rainin HPLC system - HPXL solvent delivery system capable of achieving 4000 psi. 50 µL sample loop. Knauer variable wavelength UV detector. Dynamax automatic sample injector. Digital integrator: EZChrom.
Waters System:	Waters 712 WISP Sample Processor or equivalent. 50 µL sample loop or equivalent. Waters 486 tunable absorbance detector or equivalent. Waters 600E Multisolvent delivery system or equivalent. Digital Integrator: EZChrom.
Hewlett Packard System:	HP 1313A Autosampler. HP G1311A QuatPump. HP G1322A On-line degasser. HP G1316A Thermostat column compartment. HP 1314A Variable wavelength detector. Digital Integrator: EZChrom.

2.1.1 Column Temperature Control:

2.1.2 Column temperature is controlled through the use of a column heater which is maintained at a temperature of 25°C.

2.2 Standards

2.2.1 Target Analyte Stock Solution

2.2.1.1 The stock solution used contains the 14 standard compounds in the mix at a concentration of 1000 µg/mL and is generally purchased from AccuStandard Inc. (25 Science Park, New Haven CT 06511). Equivalent solutions from this or other vendors are also acceptable.

2.2.1.2 The NG and PETN stock solutions are purchased individually from AccuStandard, Inc. (25 Science Park, New Haven, CT 06511). The NG solution comes in 1 mL ampules at 4000 µg/mL in ethanol. The PETN solution comes in 1 mL ampules at 1000 µg/mL in methanol. Equivalent solutions from this or other vendors are also acceptable.

2.2.1.3 The 3,5-Dinitroaniline and 1,3,5-Trinitroso-1,3,5-hexahydrotriazine standards are made from standard analytical reference materials obtained from the U.S. Army Environmental Center (Aberdeen Proving Ground, MD 21010). The 2,4-Diamino-6-nitrotoluene, 2,6-Diamino-4-nitrotoluene and 2,2',6,6'-Tetranitro-4,4'-azoxytoluene standards are made from standard analytical reference materials obtained from AccuStandard, Inc. (25 Science Park, New Haven, CT 06511). The 1-Nitroso-3,5-dinitro-1,3,5-hexahydrotriazine standards are made from standard analytical reference materials obtained from Stanford Research.

2.2.1.4 Calibration standard, surrogate stock and IBLK surrogate solutions are detailed in Appendix I.

2.2.2 Surrogate Stock Solution

2.2.2.1 The surrogate stock solution is received in a methanolic solution at a concentration of 1000 µg/mL. The surrogate can also be prepared by weighing 100 mg of 1,2-dinitrobenzene into a 100 mL volumetric flask and diluting to volume with methanol to yield a concentration of 1000 µg/mL.

2.2.3 IBLK Working Solution

2.2.3.1 The working instrument blank solution contains the surrogate compound only at a concentration of 2.0 µg/mL. Prepare this solution by adding 100 µL of the 1000 µg/mL surrogate stock solution to a 50 mL volumetric flask. Dilute to volume so that the final solvent concentration is methanol/water at a ratio of 1:1.

2.2.4 Working Calibration Standards

2.2.4.1 Prepare the working calibration standards for the 14 standard analytes in the following manner. All solutions are prepared in acetonitrile and diluted 1:1 with water just prior to analysis. These 14 analytes are combined into one working solution, since they do not co-elute on the primary column.

Standard	Source Solution	Amount Added (mL)	Final Volume (mL)	Final Concentration (µg /mL)
Standard #6	A	0.20	10	20.0
	B	0.20		
Standard #5	A	0.1	10	10.0
	B	0.1		
Standard #4	C	1.0	10	2.0
Standard #3	D	1.0	10	1.0
Standard #2	E	1.0	10	0.2
Standard #1	F	1.0	10	0.1

Source Solution	Concentration (µg /mL)
A = 14 Component Mix	1000
B = Surrogate Stock Solution	1000
C = Standard #6	20
D = Standard #5	10
E = Standard #4	2.0
F = Standard #3	1.0

2.2.4.2 Prepare the working calibration standards for the 6 additional analytes in the following manner. All solutions are prepared in acetonitrile and diluted 1:1 with water just prior to analysis.

Standard	Source Solution	Amount Added (mL)	Final Volume (mL)	Final Concentrations (µg /mL)
Standard #6	A	2.0	10	20.0
	B	0.2		
	C	0.2		
	D	0.2		
	E	0.2		
	F	2.0		
	G	0.2		
Standard #5	H	5.0	10	10.0
Standard #4	H	1.0	10	2.0
Standard #3	I	1.0	10	1.0
Standard #2	J	1.0	10	0.2
Standard #1	K	1.0	10	0.1

Source Solution	Concentration (µg/mL)
A = MNX	100
B = TNX	1000
C = 3,5-DNA	1000
D = 2,6-DA-4-NT	1000
E = 2,4-DA-6-NT	1000
F = 4,4'-TN-AZOXY	100
G = 1,2-DNB	1000
H = Standard 6	20.0
I = Standard 5	10.0
J = Standard 4	2.0
K = Standard 3	1.0

2.2.4.3 Prepare the working calibration standards for PETN/NG in the following manner. All solutions are prepared in a 1:1 acetonitrile/water mixture.

Standard	Source Solution	Amount Added (mL)	Final Volume (mL)	Final Concentrations NG:PETN:1,2-DNB (µg /mL)
Standard #5	A	0.05	10	20.0
	B	0.10	10	10.0
	C	0.10	10	10.0
Standard #4	D	5.0	10	10.0, 5.0, 5.0
Standard #3	E	5.0	10	5.0, 2.5, 2.5
Standard #2	F	2.0	10	1.0, 0.5, 0.5
Standard #1	G	5.0	10.0	0.5, 0.25, 0.25

Source Solution	Concentration (µg/mL)
A = Nitroglycerin	4000
B = PETN Solution	1000
C = Surrogate Stock Solution	1000
D = Standard 5	As Above
E = Standard 4	As Above
F = Standard 3	As Above
G = Standard 2	As Above

2.2.4.4 Note: Store all standard and surrogate solutions in amber glass vials with screw caps and Teflon-lined septa. Minimize headspace in these vials and store them in a refrigerator kept at 4°C ±2°C. Allow standards to come to room temperature prior to use.

2.2.4.5 Stock solutions may be used for up to one year, and working solutions are good for at least six months, or the expiration date of the parent standard, whichever is sooner.

2.2.4.6 All standards are assigned a unique identifier to enable cross-referencing of each individual standard back to the supplier's lot number. In addition, all standards are labeled with the standard concentration, the solvent, date prepared, expiration date, analyst's initials, and the standard reference number. Refer to Laucks' SOP on the traceability, documentation, and preparation standards.

3. Safety precautions

3.1 Routine Safety Precautions

3.1.1 All standards and sample extracts should be handled as if they are hazardous substances.

3.1.2 All compounds analyzed by this method are used either in the manufacture of explosives or are the degradation products of these compounds. When making stock solutions for calibration, treat each explosive compound with caution.

3.1.3 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.4 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.5 Electrical shock - All instruments present the possibility of electrical shock. The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.6 Almost all of the analytes under consideration are known or suspected carcinogens. Analysts should wash their hands after using any standard, solvent or sample extract. Additionally, a respirator should be worn or a fume hood utilized for extremely hazardous compounds or very dirty extracts.

3.2 Waste disposal

3.2.1 Out of date standards and sample extracts are disposed of in the designated organic waste container located in the organic preparation area.

3.2.2 HPLC liquid waste is disposed of by pouring into the designated organic waste container located in the solvent storage area.

4. Operation procedures

4.1 Analytical Conditions

4.1.1 Current C18 Column Conditions for the 14 Compounds:

HPLC3		HPLC4	
Pump A Solvent:	Methanol	Solvent:	Methanol/Water
Pump B Solvent:	Water	Flow:	0-24 min = 0.5 mL/min
Flow:	1.0 mL/minute:		24-35 min = 0.8 mL/min
Gradient:	Linear		35-40 min = 0.5 mL/min
Run Time:	60 minutes	Run Time:	40 minutes
Acquisition Time:	60 minutes	Acq. Time:	35 minutes
Injection Volume:	50 µL inj.	Time:	50 µL

Gradient Profile (HPLC3)		**Run Time Profile**
Initial %A:	40	
Initial %B:	60	
Hold Time:	5 minutes	0 - 5 minutes
Gradient 1 %A:	60	
Gradient 1 %B:	40	
Ramp Time 1:	15 minutes	
Hold Time 1 :	5 minutes	5 - 20 minutes
Gradient 2 %A:	95	
Gradient 2 %B:	05	
Ramp Time 2:	10 minutes	20 - 30 minutes
Hold Time 2:	5 minutes	30 - 35 minutes
Gradient 3 %A:	40	
Gradient 3 %B:	60	
Ramp Time 3:	5 minutes	35 - 40 minutes
Hold Time 3:	20 minutes	40 - 60 minutes (Column Equilibration)

4.1.2 Current CN/C8 Column Conditions for the 14 Compounds:

HPLC4 File #5:

Pump A Solvent:	Methanol
Pump B Solvent:	Water/0.05% H_3PO_4 buffer
Pump C Solvent:	Acetonitrile
Flow:	0.85 mL/minute
Gradient:	Linear
Run Time:	80 minutes
Acquisition Time:	60 minutes

Initial %A	12
Initial %B	86 (Hold time initial 15 min. Flow ramps to 0.85 mL/min.)
Initial %C	2

Gradient 1 %A:	30	
Gradient 1 %B:	68	
Gradient 1 %B:	2	
Ramp Time 1:	25 minutes	15 - 40 minutes

Gradient 2 %A:	60	
Gradient 2 %B:	40	
Ramp Time 2:	2 minutes	40 - 42 minutes
Hold Time 2 :	38 minutes	42 - 80 minutes

4.1.3 Current C18 Column Conditions for the 6 Additional Compounds:

Gradient Profile (HPLC3)		**Run Time Profile**
HPLC3 File:	EXTRAS	
Pump A Solvent:	Water	
Pump B Solvent:	Methanol	
Flow:	1.0 mL/minute	
Gradient:	Linear	
Run Time:	53 minutes	
Acquisition Time:	30 minutes	
Initial %A	90	
Initial %B	10	
Gradient 1 %A:	70	
Gradient 1 %B:	30	
Ramp Time 1:	5 minutes	0 - 5 minutes
Hold Time 1 :	0 minutes	
Gradient 2 %A:	50	
Gradient 2 %B:	50	
Ramp Time 2:	3 minutes	5 - 8 minutes
Hold Time 2 :	7 minutes	8 - 15 minutes
Gradient 3 %A:	26	
Gradient 3 %B:	74	
Ramp Time 3:	2 minutes	15 - 17 minutes
Hold Time 3:	13 minutes	17 - 30 minutes
Gradient 4 %A:	90	
Gradient 4 %B:	10	
Ramp Time 4:	2 minutes	30 - 32 minutes
Hold Time 4:	21 minutes	32 - 53 minutes (Column Equilibration)

4.1.4 Current CN/C8 Column Conditions for the 6 Additional Compounds:

Time	Flow	Methanol	Water
	1.0	15	85
2.4	1.0	15	85
7.0	1.0	40	60
10.0	1.0	50	50
17.0	1.0	50	50
20.0	1.0	80	20
21.0	0	15	85

4.1.5 Current Column Conditions for NG/PETN:

C18		CN	
Pump A Solvent:	Methanol	Pump A Solvent:	Methanol
Pump B Solvent:	Water	Pump B Solvent	Water
Flow:	0.6 mL/minute:	Flow:	1.2 mL/minute
Gradient:	Linear (1:1)	Gradient:	Linear (1:1)
Run Time:	30 minutes	Run Time:	20 minutes
Acquisition Time:	30 minutes	Acq. Time:	20 minutes
Injection Volume:	50 µL inj.	Time:	50 µL

4.2 Method Detection Limit Study

4.2.1 Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in the Laucks SOP on determination of detection limits. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration near the anticipated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL. MDL studies are performed on both columns.

4.3 Method Validation

4.3.1 Prior to the analysis of any samples, it is necessary to validate the method. A method validation study is performed in a similar manner to an MDL study with the exception that a minimum of 4 replicates are required and the concentration levels are typically higher.

4.4 Retention Time Windows

4.4.1 It is necessary to establish retention time windows for the method by analyzing standards for all target analytes over at least a 24-hour period. A 24-hour time period may be deemed more appropriate for this analysis because the instrument is not always operated for longer periods when analyzing sample extracts. At least 5 standards must be injected during the 24-hour time period, at about equal time intervals. These standards should be interspersed with real sample extracts in order to mimic actual instrument operating conditions. Tabulate the retention times for all standard compounds and compute the sample (n-1) standard deviations of all the retention times.

4.4.2 The retention time window half-width is set at 3 times the above calculated standard deviation. This operation must be repeated whenever major equipment changes are made or whenever the chromatographic method is modified.

4.4.3 In some cases, the retention time window may be modified in order to take into account any pattern shifting. This shift is acknowledged by observation of the surrogate peak behavior and the surrounding CCV standards. If retention time shift has occurred and the possibility of misidentifying peaks exists, then the sample is reanalyzed bracketed by in-control CCV standards.

4.4.4 See the Laucks SOP on determination of retention time windows for more specifics on their determination and use.

4.5 Initial Multi-Point Calibration

4.5.1 Analyze standard solutions (including the surrogate solution) using at least 5 different concentration levels. The lowest concentration defines the reporting limit. The highest concentration should define the upper usable working range of the detector. Inject the standard solutions from the lowest concentration to the highest. Criteria for evaluating these standards are detailed in Section VI.

4.6 Initial Calibration Verification

4.6.1 At the beginning of an analysis sequence, analyze the mid-point calibration standard (STD 3). The computed calibration factor (CF) or concentration measurement must meet the criteria detailed in Section VI.

4.6.2 Since the retention time windows which were established by the retention time study are relative and not absolute, the windows are anchored by the ICV. This allows the retention times from the ICV to become the mid-point of the retention time windows.

4.7 Instrument Blank

4.7.1 After the analysis of Standard 5, an instrument blank (IBLK) is analyzed. This is to verify that there is no carryover between sample injections. Evaluation criteria are detailed in Section VI.

4.7.2 Any sample that is suspected of containing high concentrations of target analytes should be followed by an IBLK. This IBLK analysis is used only to make a judgment as to the possibility of carryover into the sample analysis immediately following the IBLK. Evaluation criteria are detailed in Section VI.

4.8 Continuing Calibration Verification

4.8.1 A mid-range calibration standard (STD 3) is analyzed after every ten sample injections. In addition, this standard must be the last injection made in the analysis sequence. Evaluation criteria are detailed in Section VI.

4.9 Sample Analysis

4.9.1 Analysis sequence

See Appendix II for a detailed analysis injection sequence.

4.9.2 Compound Identification

4.9.2.1 Compounds are tentatively identified if a peak elutes in the retention time window characteristic of that compound on the primary column. To confirm the presence of that compound in the sample extract, the peak must also elute in its retention time window on a second column. Currently, separation of the ordnance compounds is achievable. However, when there are analyte co-elutions on the secondary column, the responses are no longer summed. Instead, separate individual standards are analyzed and the sample results are still flagged appropriately. All analyte quantitations come from the C18 column. The CN/C8 columns in series are typically not used for quantitation purposes. Retention time windows are established as previously described and are updated each QC period. Compounds can only be identified if the ICV and CCV criteria detailed in Section VI are strictly adhered to. Due to constraints of the software, the RT of the co-eluting compounds is determined by assigning the RT to the highest point within a give window. For the co-eluting compounds that may have a slight but not complete separation, such as: 2-nitrotoluene, 3-nitrotoluene and 4-nitrotoluene, this determination of RT can result in RT windows which exceed those identified by the standard (due to the changes in peak heights with concentration values). In order to avoid potential

exceedance of RT windows, and in order to accurately identify these co-eluting target analytes, the retention time windows may be administratively set for the co-eluting compounds.

4.9.2.2 The experienced analyst's judgment weighs heavily in evaluating chromatograms for compound identification. For instance, the retention times of surrogate compounds may be outside their expected windows due to sample matrix effects. The analyst may decide to re-adjust the target analyte's retention time windows on an ad hoc basis based on such an observed shift. This can occur only on a sample-specific basis and is used when the analyst examining the data suspects that a retention time shift has occurred. If this is done, it must be fully documented in the case narrative notes. If the concentration of any target analyte exceeds the calibration range, the sample extract must be diluted and reanalyzed.

4.9.3 Compound Quantification

4.9.3.1 Target compound concentrations are calculated using the following equations:

4.9.3.2 Aqueous samples

The external standard equation, as expressed in SW-846 is

$$Concentration(\mu g / L) = \frac{A_x \times A \times V_i \times D}{A_s \times V_i \times V_s}$$

where:

A_x = Response for the analyte in the extract, in area or height units.
A = Amount of standard injected (in nanograms).
A_s = Response for the external standard, same units as A_x.
V_i = Volume of extract injected, µL.
D = Dilution factor of extract. The final result of an algebraic multiplication of the ratio of all dilution final volumes to initial volumes. For example, if an extract is diluted 10 µL to 1000 µL and subsequently diluted an additional 10 µL to 1000 µL, the expression is: (1000/10) * (1000/10) = 100 * 100 = 10,000. If no dilution was made, D = 1.
V_t = Volume of total extract, µL.
V_s = Initial sample size, mL.

4.9.3.3 In routine use at Laucks, the equation reduces as follows.

4.9.3.4 First, CF is used directly in the equation. Since $Cf = A_s/A$, this substitution is made. Next, since Laucks routinely measures all final extract volumes in mL, a conversion factor for µL to mL must be made in the numerator of the expression - i.e., V_t = 1000 * mL. Finally, the

sample preparation process is represented as the algebraic ratio of initial sample size to final extract volume.

4.9.3.5 The equation then becomes

$$Concentration(\mu g / L) = \frac{1000 \times Ax \times D}{CF \times Vi \times (Vs / Vt)}$$

4.9.3.6 This expression is completely equivalent to the SW-846 equation, yielding the same final result. To report concentrations in alternate units, apply an appropriate factor:

mg/L = µg/L * 0.001

4.9.3.7 Non-aqueous samples

4.9.3.8 The results calculation for non-aqueous samples is very similar to that for aqueous samples. The only difference is the inclusion of a total solids term to calculate the dry weight equivalent of the initial sample size.

$$Concentration(\mu g / kg) = \frac{1000 \times A_x \times D}{CF \times V_i \times (W / V_t) \times T_s}$$

where:

W_s = Sample size extracted in grams.
T_s = Total Solids in decimal format (i.e. 0.76 not 76).

5. Reports

5.1 Data Packet Organization

See Appendix III for a check list detailing data packet organization.

5.2 Quality Control Reports

5.2.1 All results for quality control tests are entered into the lab data base. Printouts of all data entered must be included in the data packet. The routine minimum is a method blank report, a method blank spike report, and an MS/MSD report.

5.3 Data Qualifying Flags

5.3.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

U:	The analyte of interest was not detected, to the limit of detection indicated.
B:	The analyte of interest was detected in the method blank associated with the sample, as well as in the sample itself. The B flag is applied without regard to the relative concentrations detected in the blank and sample.
J:	The analyte of interest was detected below the practical quantitation limit. This value should be regarded as an estimate.
D:	The value reported is derived from the analysis of a diluted sample or sample extract.
P:	When a dual column technique is employed, this flag indicates that calculated results from the two columns differ by more than 25 percent.
E:	The value reported is based on a sample or sample extract in which the target analyte concentration exceeded the calibration range. The value reported should be considered an estimate.
X:	The sample has been analyzed at several dilutions. The value reported has been determined to be the most appropriate quantitative value.
Z:	The value reported is from the C18 column and theres is coelution with another target analyte on the CN/C8 columns in series.

6. Quality Control

See the Requirements and Corrective Actions table in Appendix IV for additional information.

6.1 Initial Calibration

6.1.1 Criteria

6.1.1.1 The initial calibration is evaluated by calculating the %RSD of the calibration factors from the five linearity standards.

6.1.1.2 CFs are calculated using the equation:

$$CF = \frac{\text{response}}{\text{ng injected}}$$

6.1.1.3 This %RSD method assumes a linear response with the calibration curve passing through the origin.

6.1.1.4 The calculated CFs are tabulated and the %RSDs calculated. All compounds must have a %RSD of 20% to meet the method criteria.

6.1.2 Corrective action

6.1.2.1 If the %RSD criteria of 20% are not met, the out of control standard should be reanalyzed. If the curve is still out of control, determine the cause of failure and correct. Recalibrate the instrument and reanalyze any samples associated with the out of control curve.

6.2 Initial Calibration Verification

6.2.1 Criteria

6.2.1.1 Using the average CF calculation technique, compute the CFs for each compound. The calibration factors for the ICV standard are compared to the mean CFs for the initial multi-point calibration. The percent difference for these calibration factors is calculated as follows:

$$\%\,Difference = \frac{CF_a - CF_i}{CF_a} \times 100$$

where:
CF_a = .Average CF from the initial multi-point calibration
CF_i = Calibration Factor of the calibration verification standard.

6.2.1.2 The %D cannot exceed 15% for any target analytes or surrogates.

6.2.1.3 The mid-point for the RT window of each compound is updated using the ICV RTs.

6.2.2 Corrective action

6.2.2.1 If the ICV criteria are not met, no sample extracts can be analyzed. Determine the cause of the ICV failure and correct. Reanalyze the ICV and if it is still out of control, a new calibration curve must be analyzed.

6.3 Continuing Calibration Verification

6.3.1 Criteria

6.3.1.1 A CCV standard is analyzed singly for every 10 injections, and after the last sample of the sequence. The CF for each compound is calculated and the percent difference is calculated as shown above.

6.3.1.2 The %D results cannot exceed 15% for any target analytes or surrogates.

6.3.1.3 The retention times for all target analytes must fall within the RT windows established by the ICV.

6.3.2 Corrective action

6.3.2.1 Determine the cause of failure and correct. Reanalyze the calibration curve. All samples bracketed by an out of control CCV must be reanalyzed unless the CCV demonstrates an

increase in response and no analytes are detected above the reporting limit in the associated samples.

6.4 Instrument Blank

6.4.1 Criteria

6.4.1.1 There must be no target analyte levels above half the reporting limit in the initial IBLK.

6.4.2 Corrective action

6.4.2.1 If the initial IBLK contains measurable levels of target analytes, the system is out of control. The source of contamination must be identified and corrected.

6.4.2.2 IBLKs are used to monitor for possible carryover in high concentration extracts. Those IBLKs optionally placed into the sequence following suspected high concentration extracts are used to flag the possibility of analyte carryover into the following sample extract. The extract immediately following the out of control IBLK may need to be reanalyzed if there is a detectable amount of the analyte found in the IBLK.

6.5 Method Blank

6.5.1 Criteria

6.5.1.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples extracted at the same time or at least one blank for every 20 samples, whichever is more frequent. Analytes of interest should not be detected at levels greater than half the current reporting limit, or less than 5% the regulatory limit, or less than 5% of the sample result for the same analyte. If any analytes are detected above half the reporting limit, corrective action must be taken.

6.5.2 Corrective action

6.5.2.1 Steps shall be taken to find/reduce/eliminate the source of the contamination. Sample corrective action may be limited to qualification for blank contamination. When the concentrations of any target analytes in the method blank are above 1/2 the reporting limit for the majority of target analytes or above the reporting limit for target analytes known to be common laboratory contaminants, the effect this may have had on the samples will be assessed. If any analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps shall be taken to find/reduce/eliminate the source in the method blank. The case narrative should aso discuss the situation. If an analyte is found in the method blank and some, or all, of the other batch samples, additional corrective action is required to

reanalyze the method blank and any samples containing the same contaminant. If the contamination remains, the contaminated samples of the batch would be reprepared and reanalyzed with a new method blank and batch specific QC samples. Sporadic cases of contamination may be difficult to control, however, daily contamination would not be acceptable.

6.6 Blank Spike or QC Check Sample (LCS)

6.6.1 Criteria

6.6.1.1 A blank spike follows the same protocol as the matrix spike analysis except that the spiking solution is added to a method blank solution instead of an actual sample. In addition, this spiking solution is supplied from a source other than the calibration standards. The use of a second source for the spiking standards is employed in order to verify the calibration standards. A method blank with added analytes is a blank spike. Blank spike percent recovery control limits are detailed in the laboratory QC database. These control limits are updated periodically.

6.6.2 Corrective action

6.6.2.1 The blank spike is used to determine whether a method is in control during sample preparation and analysis. Sample re-extraction and reanalysis would be triggered by any analytes falling outside of control limits in the blank spike sample unless all sample surrogate recoveries and MS/MSD spike recoveries are in control.

6.7 Matrix Spike

6.7.1 Criteria

6.7.1.1 A sample is chosen at random (unless designated by project-specific requirements) from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to extraction. It is required that a matrix spike analysis be performed with each extraction batch. However, the minimum frequency for MS analysis is 1 each per 20 samples per matrix. This frequency may be changed on a project specific basis. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. This spiking solution is supplied from a source other than the calibration standards. The use of a second source for the spiking standards is employed in order to verify the calibration standards. The recovery of spike analytes is calculated as follows:

$$\%Recovery = \frac{SSR - SR}{SA} \times 100$$

where:
SSR = Concentration in spiked sample.
SR = Native concentration in unspiked sample.
SA = Concentration of spike added.

6.7.1.2 The current recovery criteria are detailed in the Laucks quality control database. These control limits are updated periodically.

6.7.2 Corrective action

6.7.2.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action may involve recalculation, re-extraction and/or reanalysis. This process should also look at the recovery of surrogate compounds in the MS sample and at the recovery of matrix spiking compounds from the extraction batch blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

6.8 Matrix Spike Duplicate

6.8.1 Criteria

6.8.1.1 The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used to measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values. This calculation is as follows:

$$RPD = \frac{S1 - S2}{(S1 + S2)/2} \times 100$$

where:
S1 = Measured concentration for MS sample.
S2 = Measured concentration for MSD sample.

6.8.1.2 The current RPD control limits are detailed in the Laucks quality control database. These control limits are updated periodically.

6.8.2 Corrective action

If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility.

6.9 Surrogate Recovery

6.9.1 Criteria

6.9.1.1 Surrogates are chemically similar compounds added to every sample, method blank, and QC sample prior to sample processing. They are used to monitor for potential sample processing errors and matrix effects. Surrogate compound recoveries are calculated as follows:

$$\%Recovery = \frac{S_m}{S_a} \times 100$$

where:
S_m = Concentration of surrogate measured in sample.
S_a = Concentration of surrogate added.

6.9.1.2 Detailed surrogate recovery control limits are detailed in the Laucks quality control database. These control limits are updated periodically.

6.9.2 Corrective Action

6.9.2.1 Reanalyze the sample. Low surrogate recoveries are greater potential indicators of poor method performance than high surrogate recoveries since non-GC/MS methods cannot separate co-eluting interferents. In instances where high surrogate recoveries are attributable to matrix effects, no corrective action is taken. However, if elevated surrogate recoveries are attributable to preparation error, re-extraction and reanalysis is performed.

6.9.2.2 Check calculations for possible error. Re-extract the sample if surrogate recovery is less than the lower control limit. If a poor injection is suspected, reanalyze the sample.

6.9.2.3 Low surrogate recoveries in the method blank may require that all the samples in the associated batch be re-extracted and reanalyzed. In any case, it is imperative to identify the problem associated with low recovery so that it can be corrected. It is a requirement that all out of control surrogate recoveries and the corrective action taken be discussed in the narrative.

7. References

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Method 8000B, "Gas Chromatography," Revision 1, July 1992, U.S.E.P.A.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 4th Update, Method 8330A, "Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)," Revision 1, January 1998, U.S.E.P.A.

40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984, U.S.E.P.A.

Special Report 93-11, "Experimental Assessment of Analytical Holding Times for Nitroaromatic and Nitroamine Explosives in Soil," Clarence L. Grant et al, June 1993, U.S. Army Cold Regions Research and Engineering Laboratory.

Special Report 93-24, "Evaluation of Pre-extraction Analytical Holding Times for Nitroaromatic and Nitroamine Explosives in Water," Clarence L. Grant et al, August 1993, U.S. Army Cold Regions Research and Engineering Laboratory.

APPENDIX I

Calibration Standard Solution Concentrations, µg/mL

Compound	STD1	STD2	STD3	STD4	STD5	STD6
HMX	0.1	0.2	1.0	2.0	10.0	20.0
RDX	0.1	0.2	1.0	2.0	10.0	20.0
1,3,5-TNB	0.1	0.2	1.0	2.0	10.0	20.0
1,3-DNB	0.1	0.2	1.0	2.0	10.0	20.0
Tetryl	0.1	0.2	1.0	2.0	10.0	20.0
NB	0.1	0.2	1.0	2.0	10.0	20.0
2,4,6-TNT	0.1	0.2	1.0	2.0	10.0	20.0
4-Am-DNT	0.1	0.2	1.0	2.0	10.0	20.0
2-Am-DNT	0.1	0.2	1.0	2.0	10.0	20.0
2,4-DNT	0.1	0.2	1.0	2.0	10.0	20.0
2,6-DNT	0.1	0.2	1.0	2.0	10.0	20.0
2-NT	0.1	0.2	1.0	2.0	10.0	20.0
3-NT	0.1	0.2	1.0	2.0	10.0	20.0
4-NT	0.1	0.2	1.0	2.0	10.0	20.0
Surrogate						
1,2-Dinitrobenzene	0.1	0.2	1.0	2.0	10.0	20.0

Calibration Standard Solution Concentrations, µg/mL

Compound	STD1	STD2	STD3	STD4	STD5	STD6
TNX	0.1	0.2	1.0	2.0	10.0	20.0
2,6-DA-4-NT	0.1	0.2	1.0	2.0	10.0	20.0
2,4-DA-4-NT	0.1	0.2	1.0	2.0	10.0	20.0
MNX	0.1	0.2	1.0	2.0	10.0	20.0
3,5-DNA	0.1	0.2	1.0	2.0	10.0	20.0
4,4'-TN-AZOXY	0.1	0.2	1.0	2.0	10.0	20.0
Surrogate						
1,2-Dinitrobenzene	0.1	0.2	1.0	2.0	10.0	20.0

Calibration Standard Solution Concentrations, µg/mL

Compound	STD1	STD2	STD3	STD4	STD5
NG	0.5	1.0	5.0	10.0	20.0
PETN	0.25	0.5	2.5	5.0	10.0
Surrogate					
1,2-Dinitrobenzene	0.25	0.5	2.5	5.0	10.0

Surrogate Stock Solution

Compound	Concentration
1,2-Dinitrobenzene	1000 µg/mL

IBLK Solution

Compound	Concentration
1,2-Dinitrobenzene	2.0 µg/mL

APPENDIX II

Analysis Sequence

Injection	Sample
1	Standard #1
2	Standard #2
3	Standard #3
4	Standard #4(ICV Standard)
5	Standard #5
6	Standard #6
7	IBLK
8	ICV
	injections (9-16)
17	IBLK
18	CCV Standard
19	injections (19-27)
28	BLK
29	CCV Standard
	injections (total of 10 injections between CCVs)
last	IBLK
last	CCV Standard

APPENDIX III

Data Packet Order List

I. QC SUMMARY

Surrogate Recovery Summary Report
Blank Spike Report
MS/MSD Report
Method Blank Summary

II. SAMPLE DATA:

Organic Analysis Data Sheet
Sample Confirmation Worksheet
Chromatogram, primary column
Quantitation Report, primary column
Chromatogram, secondary column
Quantitation Report, secondary column

III. STANDARD DATA:

Linearity Report
ICAL Data
ICAL Response, ICAL std concentrations
ICV reports
CCV reports
Other Standards Used to Support Sample Data and Instrument Blanks

V. Raw QC Data:

Method Blank
Chromatograms
Quantitation Report

Blank Spike
Chromatograms,
Quantitation Report

Matrix Spike
Chromatograms
Quantitation Report

Matrix Spike Duplicate
Chromatograms
Quantitation Report

V. Bench Sheets

SDG Report
Extraction Bench Sheets
Injection Sequence (logbook copy)
Miscellaneous Work Sheets. (%TS, calcs, HTVRs)
Standards Logs

VI. Reject Data:

Data not used to support reported sample results.
All data acquired but rejected on account of QC out of control.
Non-routine standards used to support sample data should be placed at the last of the Standard Data section.

APPENDIX IV

Method 8330 Requirements and Corrective Actions					
QA Element	**Method Criterion**	**Laucks Criterion**	**Frequency**	**Corrective Action**	**Documentation**
Initial Calibration	Minimum of 5 levels.	Minimum of 5 levels. Must demonstrate an RSD of <20%.	As necessary due to major instrument maintenance or difficulties meeting the CCV requirements.	Reanalyze out of control standard. If still out, determine cause of curve failure and correct. Re-analyze curve and any samples analyzed against curve.	Target forms and raw data.
Initial Calibration Verification	+/- 15% of the initial calibration response factor.	+/- 15% of the initial calibration response factor.	Every 24 hr. or at the beginning of an analytical sequence, which ever is more frequent, or as necessary.	Determine cause of ICV failure and correct. Reanalyze ICV and if out of control a new calibration curve must be analyzed.	Target form and raw data.
Continuing Calibration Verification	+/- 15% of the initial calibration response factor. Analyze singly every 10 injections and after the final sample.	+/- 15% of the initial calibration response factor.	Every 10 injections and at the end of an analytical sequence.	Determine cause of failure and correct. Reanalyze calibration curve. All samples bracketed by an out of control CCV must be reanalyzed unless the CCV demonstrates an increase in response and no analytes are detected above the reporting limit.	Target form and raw data.
Instrument Blank	Analyze after analysis of a sample with analyte levels which exceed the upper calibration level.	Analyze after samples when high levels of matrix are suspected.	As necessary.	Reanalyze any samples with suspected carryover.	Raw data
Method Blank	All analytes must be < MDL	All analytes must be less than half the Reporting Limit, or <5% regulatory limit, or <5% of the sample result, whichever is greater.	One method blank per 20 samples or each extraction batch, whichever is more frequent.	Reanalyze blank. If still out of control. re-extract the entire batch of samples unless the detected analyte(s) are not present in the associated samples.	Method Blank Summary and raw data. Narrative comment when necessary.

Method 8330 Requirements and Corrective Actions					
QA Element	**Method Criterion**	**Laucks Criterion**	**Frequency**	**Corrective Action**	**Documentation**
Surrogate Recovery	Minimum of 1 surrogate. Recoveries must fall within the labs established windows.	See latest version of Laucks Testing Labs control limits catalogue. All surrogate recoveries must fall within the generated limits. If laboratory limits are not established due to the implementation of a new surrogate , the default limits of 70% - 130% are used until enough data points are collected to generate new limits.	All samples, method blanks, and QC samples.	Re-extract if surrogate recovery is < the lower control limit. If a poor injection is suspected reanalyze the sample.	Target Surrogate Summary form or special test results. Narrative comment when necessary.
MS/MSD	One per 20 samples or extraction batch which ever is more frequent. Must be per matrix.	See latest version of Laucks control limits located in the QC database.	1 MS/MSD pair per 20 samples or every extraction batch which ever is more frequent.	Per SW 846, if analyte recoveries are out of control in the MS/MSD but are in control in the associated blank spike, no further action is required.	MS/MSD report and raw data. Narrative comment when necessary.
Blank Spike	N/A	See latest version of Laucks Testing Labs control limits in the QC database. All recoveries must fall within the generated limits.	1 per 20 samples or every extraction batch which ever is more frequent.	Re-extract if analyte recoveries are outside of control limits.	Blank Spike report and raw data. Narrative comment when necessary.

APPENDIX V

Elution Order of Target Analytes

Compound	Order of Elution on Primary (C18) Column	Order of Elution on Confirmation (CN/C8) Column
HMX	1	7
RDX	2	4
1,3,5-TNB*	3	1
1,3-DNB	5	2
Tetryl	7	14
NB*	6	3
2,4,6-TNT*	8	6
4-Am-DNT	9	14
2-Am-DNT	10	12
2,4-DNT*	11	8
2,6-DNT*	12	9
2-NT*	13	10
3-NT*	14	13
4-NT*	15	11
Surrogate		
1,2-Dinitrobenzene	4	5

Elution Order of 6 Additional Analytes

Compound	Order of Elution on Primary (C18) Column	Order of Elution on Confirmation (C8/CN) Column
TNX	3	1
2,6-DA-4-NT	2	2
2,4-DA-6-NT	1	3
MNX	4	4
3,5-DNA	6	5
4,4'-TN-AZOXY	7	6
Surrogate		
1,2-Dinitrobenzene	5	5

Elution Order of PETN/NG

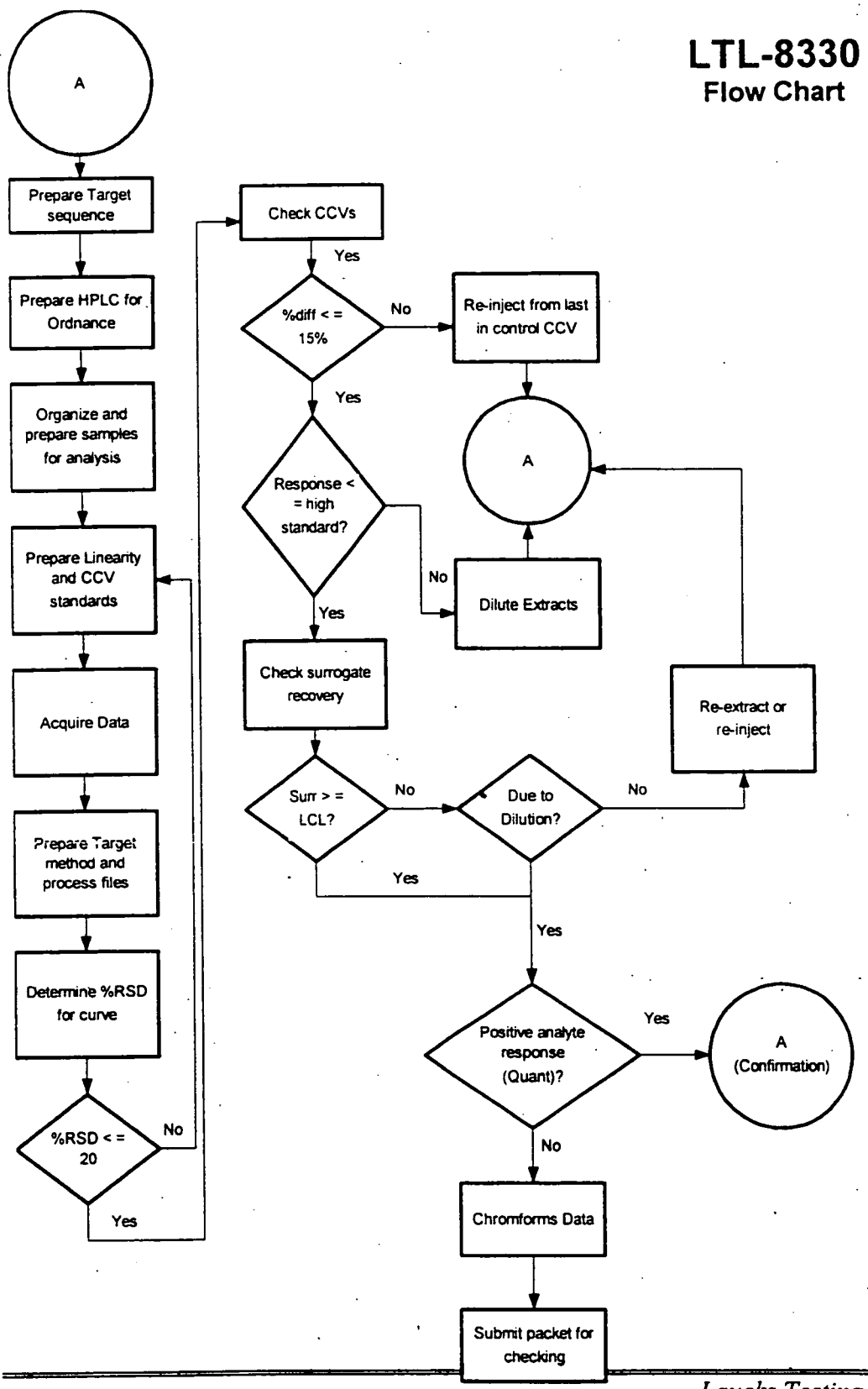
Compound	Order of Elution on Primary (C18) Column	Order of Elution on Confirmation (CN) Column
NG	2	2
PETN	3	3
Surrogate		
1,2-Dinitrobenzene	1	1

*Indicates the compound co-elutes on the confirmation (CN) column.

APPENDIX VI

Method 8330 Flow Chart

LTL-8330
Flow Chart



LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP : LTL-9104

Title: **Preparation and Analysis of Total and Amenable Cyanide according to EPA Methods 335.1, 335.3, and SW 846 method 9012A.**

Revision history:

Number	Date
2	02/09/98
1	02/07/96

UNCONTROLLED

Revised by: Bill Lundberg, Division Manager Date: 2/9/98

Reviewed by: Harry Romberg, QC Officer Date: 2-9-98

Approved by: Karen Kotz, Laboratory Director Date: 2/9/98

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1. Introduction and Scope

1.1 Method Description

Cyanide in samples is determined by a preparation with manual distillation followed by an automated spectrophotometric analysis on an auto analyzer with a UV digester and in-line distillation. The routine reporting limit is 10 µg/L in waters, and 0.50 mg/kg DB in soils and sediments. Pretreatment for the determination of cyanides amenable to chlorination in waters is also included in this SOP.

This SOP is applicable to the sample preparation (for cyanide analysis) of drinking waters, surface and saline waters, domestic and industrial wastes according to EPA methods 335.1, 335.3 and SW 846 method 9012A with the main difference being the use of the in-line still and UV digestion in EPA 335.3. Also, MIDI distillation with a 50 mL water sample instead of the normal distillation of a 500 mL sample is used in this SOP. Other differences from 9012A are listed on the QA chart at the end of this SOP. Soils and sediments are MIDI distilled as a 1 g sample.

This method is restricted to use by, or under the supervision of analysts experienced in the technique described and in SW 846 methodology. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Method Deviations and Comments

The following items represent deviations of Method 9012A, as published, which are followed as standard operating procedures in the performance of this method at Laucks:

- The MIDI distillation procedure is used, exactly as written in the CLP statement of work. This distillation uses a 50 mL aliquot of sample and a final distillation volume of 50 mls. This procedure allows the lab to use less sample, and dispose of smaller volumes of waste material. All molar ratios in this distillation are identical to the method as written.

- The calibration curve specified in 9012A is reduced by 2 to compensate for the lack of sample concentration in the distillation step.

1.3 Method Summary

Sample Preparation: The MIDI distillation procedure applies to relatively solid samples such as soils, sediments and sludges, or if requested to water samples. Cyanide determined by this method is defined as cyanide ion and complex cyanides converted to hydrocyanic acid by

reaction in a reflux system with mineral acid in the presence of magnesium ion. The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a MIDI reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide in the distillate is then determined in a spectrophotometric analysis.

Water samples analyzed under EPA 335.3 are not externally distilled and are directly analyzed unless otherwise requested.

Spectrophotometric Analysis: On a Technicon auto analyzer, the samples are acidified and passed through a UV digester and then distilled in-line. The cyanide released is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at pH less than 8 without hydrolysis to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 570 nm. To obtain colors of comparable intensity, it is essential to have the same salt content in both the samples and the standards.

1.4 Sample Handling, Sample Storage, Holding Times

Samples are preserved with 8 pellets of sodium hydroxide per liter of sample (pH > 12) at the time of collection. Samples must be stored at 4°C ± 2°C and must be analyzed within the specified holding time of 14 days from date of collection. The samples can be submitted in either plastic or glass containers. The pH is checked at the time of analysis and the client should be notified if the pH is less than 12.

Samples are to be checked for chlorine interference at the time of collection and the appropriate action should be taken (see section 5.4 on interferences).

1.5 Definition of Terms

This section defines terms and acronyms as they are used in this SOP. Other terms are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

Batch Identifier - A number given to each preparation or analysis group which uniquely identifies that batch. This number is generally the blank ID for preparation batches only preceded by an "A" rather than a "B" for inorganic batches. The preparation batch IDs are discussed in other documentation. The batch identifier for the second set of water samples analyzed on Feb 6, 1998 would be A020698AA1W02.

CCB - Continuing Calibration Blank - This is the same acronym used in the CLP program. This is a blank which is analyzed immediately after the CCV (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has maintained a stable baseline.

CCV - Continuing Calibration Verification. - This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has remained in calibration.

CLP - Contract Laboratory Program - The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.

Corr Coef, CC, r - Correlation coefficient - A measure of the "goodness of fit" of a set of data to a regression model. The closer the value is to 1, the higher the degree of confidence in the correlation.

DIW - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

ICB - Initial calibration blank - This term is borrowed from CLP. An instrument blank is made up in the same way as calibration standards, without target analytes.

ICV - Initial calibration verification - This term is borrowed from the CLP protocol. It is a standard which is analyzed at the start of each analytical run and compared to the initial calibration to determine whether the instrument calibration is accurate.

MDL - Method detection limit - The lowest concentration a sample which will yield a positive result that is greater zero at a known level of confidence. MDLs are empirically determined by Laucks.

SRM or LCS - Standard Reference Material or Laboratory Control Sample. This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This sample is used to demonstrate that the analytical system is in control.

QC period - Quality control period - An analysis sequence initiated by the analysis of one or more standards, followed by samples, and terminated with a standard and blank analysis. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP

Sequence - A set of sample extracts and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.

2. Equipment, Reagents, and Standards

2.1 Equipment

Required instrumentation includes the following:

1) Midi reflux distillation system with heating block capable of maintaining 125°C ± 5°C. We use the MIDI-VAP model MC-100 ("CYN-TEN").

2) Technicon Auto-Analyzer with in-line distillation unit and UV digester.

2.2 Reagents

1) 0.25 N NaOH: dissolve 10.0 g NaOH pellets in 1 L DIW. **CAUTION**: this reagent will get hot upon mixing!

2) $MgCl_2$ solution: dissolve 510 g $MgCl_2 \cdot 6H_2O$ and dilute to 1 L with DIW.

3) 1:1 H_2SO_4: carefully and slowly add with mixing 500 mL of conc. H_2SO_4 to 500 mL of DIW. **CAUTION**: this reagent will get **EXTREMELY** hot upon mixing! Mix in a Pyrex or equivalent container! **DO NOT ADD WATER TO ACID!**

4) Phosphate buffer: dissolve 13.6 g monobasic potassium phosphate (KH_2PO_4) and 0.28 g anhydrous dibasic sodium phosphate (Na_2HPO_4) and dilute to 1 L with DIW.

5) Chloramine -T solution: dissolve 1.0 g in 250 mL of DIW. Prepare this reagent fresh daily.

6) Color reagent: place 15 g of barbituric acid in the bottom of a container, and rinse down the sides of the container with DIW. Add 100 mL of DIW and swirl gently. Add 75 mL of pyridine and mix. Add 15 mL of conc. HCl, mix, and cool. Dilute to 1 L with DIW. This reagent should be stored at 4°C. This reagent should be made under a hood.

7) Distillation reagent: to 500 mL of DIW add 250 mL conc. H_3PO_4 and 50 mL 50% H_3PO_2 and then dilute to 1 L with DIW.

8) Sodium Hypochlorite solution: Commercial bleach such as Clorox (5.5%).

2.3 Standards

(a) Stock cyanide solution for standards and spiking, 100 mg/L CN. Place 0.2510 g of KCN and approx. 1.5 g NaOH in a 1.0 L volumetric flask and dissolve. Dilute up to the mark with DIW. Record this standard in a standards logbook. The stock standard is good for one year.

(b) Intermediate cyanide standard solution, 1.00 mg/L CN. Dilute 1.0 mL of stock standard solution (a) to 100 mL with 0.25 N NaOH. Prepare fresh solution at least weekly and record in a standards logbook.

(c) Blank solution for zero standard, blanks and diluting samples and standards: Dilute 200 µL 10 N NaOH to 100 mL with DIW. Prepare fresh solution at least weekly and as needed.

(d) Calibration standards:

Concentration (mg/L)	µLs of (b)	Final volume (mL)
0.200	1000	5.0
0.150	750	5.0
0.100	500.	5.0
0.050	250.	5.0
0.020	100	5.0
0.010	50.	5.0
0	0	5.0

All standards should be diluted up to final volume with (c) Blank solution. Standards are used up in analysis so prepare fresh standards for each analytical run.

3. Safety Precautions

Refer to the Laucks SOP on lab-safety practices and the instrument manufacturer's manual for routine instrument precautions.

All standards, samples and sample solutions should be handled as if they are hazardous substances. Some forms of cyanide can be released as a gaseous form upon acidification. Treat all samples as if they definitely contain cyanide.

Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

Electrical shock - All instruments present the possibility of electrical shock The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

Sodium hydroxide and sulfuric phosphoric acid are extreme irritants if they come in contact with skin or eyes. When using these chemicals, the analyst should wear gloves and safety glasses.

The color reagent (containing pyridine) should be prepared under a hood.

4. Calibration and Quality Control

Quality Control criteria are further detailed in Appendix I.

4.1 Method Detection Limit Study

Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in the Laucks SOP on determining detection limits. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration 1-5 times the anticipated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL. MDLs are determined annually.

4.2 Initial Multi-Point Calibration

The calibration standards listed in section 2.3 (d) should be analyzed in order from lowest concentration to highest. This calibration MUST IMMEDIATELY PRECEDE sample analysis. Initial calibration data is evaluated using the correlation coefficient of a linear regression analysis. The correlation coefficient must be 0.995 or greater. All calibration verifications and sample extract concentrations must be computed using the regression equation. If the criteria are not met, the instrument must be recalibrated.

The highest standard used in the linear regression calculation defines the upper usable working range of the instrument. Any sample concentration value that exceeds the concentration of this high standard must be diluted with blank solution (standard c) and reanalyzed.

4.3 Initial Calibration Verification

Immediately after the calibration curve, analyze an appropriate ICV. The calculated concentration of the ICV must be within ±15% of the true value. If the ICV criteria are not met, no samples can be analyzed. Perform system maintenance and re-calibrate. An LCSW is analyzed for every 20 samples per analytical run and only the first one is also an ICV.

4.4 Initial Calibration Blank

After the analysis of the ICV standard an instrument blank (ICB) is analyzed. The ICB consists of a sample of blank solution, standard (c). The levels of cyanide in the ICB must not exceed the reporting limit. If the initial ICB contains CN levels above the reporting limit, the system is out of control. The source of contamination must be identified and corrected before proceeding with the analysis. The instrument must be recalibrated.

4.5 Continuing Calibration Verification (CCV) and Blank (CCB)

The mid-range calibration standard of 0.100 mg/L is analyzed after every 10 samples (starting after the ICB) as the CCV. Immediately following the CCV, a sample of blank solution (standard (c)) is analyzed as the CCB. In addition, the CCV/CCB must be the last samples analyzed in the run.

Cyanide concentration in the CCV must fall within ± 15% of the true value. The levels of cyanide in the CCB must not exceed the reporting limit. If CCV limits are exceeded, check calculations or perform instrument maintenance. If the CCB limit is exceeded, identify the source of the contamination. No sample results may be reported that are not bracketed by a successful ICV/ICB and/or successful CCV/CCBs, and only ten samples within each successful bracket can be reported.

4.6 Preparation Blanks

For manual distillation preparation, the preparation blank (PB) consists of a 50 mL sample of DIW and is used to verify contamination free reagents and apparatus. A PB is distilled every 20 samples per analytical run. The cyanide concentration of the PB must not exceed the reporting limit. If the reporting limit is exceeded in a manually distilled PB, the lowest reportable concentration of CN in the associated samples is twenty times the PB concentration. Otherwise, all samples associated with the PB with cyanide concentrations less than twenty times the PB concentration and above the reporting limit, must be re-distilled and reanalyzed with a new PB.

For autoanalyzed water samples, a PBW is analyzed for every 20 samples (or with each SDG) analyzed. This does not include distillates from manual distillation which are represented by their distilled PB. This consists of a sample of blank solution (standard (c). If the cyanide concentration is above the reporting limit, then the blank solution is reprepared and reanalyzed as well as any samples diluted with the solution since the last PBW was checked (including the calibration). If the new PBW is in control, then the samples are verified by the new PBW. If contamination persists, then source isolated and the instrument is recalibrated and all samples are verified by the PBW are reanalyzed.

4.7 Matrix Spike

For manual distillation preparation, a sample is chosen at random from the samples to be analyzed (or a sample that is specifically requested by the client if they send excess sample volume). 50 µL of 100 mg/L CN standard solution, standard (a), is added to the 50 mL of sample prior to distillation, for a spike value of 0.100 mg/L in the 50 mL of distillate. For 9012A a 50 mL aliquot is spiked with 20 µL for a spike concentration of 0.040 mg/L The analyst must attempt to avoid selecting samples which are identified by the client as blanks. As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may also avoid selecting the most difficult sample of the batch for spiking. The minimum frequency for MS analysis is 1 each per 20 samples per matrix. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes.

For autoanalyzed water samples, the same criteria for sample selection and frequency applies. The MS is prepared by measuring out 10 mL of the selected sample, then adding 10 µL of the 100 mg/L CN standard (standard (a)) for a spike value of 0.100 mg/L. If the sample needs dilution, the diluted sample is spiked in the same manner for a spike value of 0.100 (multiplied by the dilution factor) mg/L.

The recovery of spike analytes is calculated as follows:

$$\% \text{ recovery} = \frac{(SS - S)}{SA} * 100$$

where:

SS = concentration in spiked sample
S = native concentration in unspiked sample
SA = spiked added; the amount of spiking material actually added to the sample calculated on the sample basis

If the spike recovery is not at or within the limits stated in QC-DB, an action such as re-analysis of the spike at a higher dilution, or selection of an alternate sample for spiking (if possible) is

taken. An exception to this rule is granted in situations where the blank spike is in control, or the sample concentration exceeds the spike level by a factor of four or more. In these cases, a narration is included with the data.

4.8 Matrix Spike Duplicate

For both manual distillation and autoanalysis; at least one duplicate sample per 20 samples per matrix is required. RPD values are calculated as follows:

$$RPD = \frac{|SR1 - SR2|}{(SR1 + SR2)/2} * 100$$

where:

SR1 = measured concentration in the initial spike analysis
SR2 = measured concentration in the duplicate spike analysis

The recovery and RPD must fall within the control limit stated in QC-DB.

4.9 Blank Spike

To verify the manual distillation procedure, a 50 mL sample of DIW is spiked with 50 µL of the 100 mg/L standard (standard (a)) for a spike value of 0.100 mg/L, and is distilled and analyzed with the other samples. The calculated recovery must be within the limits stated in QC-DB. The minimum frequency for the BS is one per 20 samples per analytical run.

4.10 Sample Duplicate

4.10.1.1 Sample duplicates are required. At least one duplicate sample per 20 samples per matrix is required when matrix spikes are being performed. RPD values are calculated in a manner similar to MS/MSD RPDs:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where:

S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analysis

4.10.1.2 The RPD control limits are detailed in the current Control Limits Catalog and in the Quality Control Database (QC_DB) and will change from time to time.

4.10.2 Corrective action

4.10.2.1 If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation procedures

5.1 Pre-distillation Sample Screen for Waters

Water samples are screened for sulfide and chlorine interferences prior to distillation as follows:

1) Pour a small amount of pH 4 buffer into a 1oz. plastic cup.

2) Check for the presence of sulfide with lead acetate test paper. Wet the paper with pH 4 buffer and then drop ~10 µL of sample onto it. A darkening of the paper indicates the presence of S^{2-}. If present then see Section 5.3 Interferences before proceeding with the distillation.

3) Check for the presence of chlorine with potassium iodide-starch test paper. Wet the paper with pH 4 buffer and then drop ~10 µL of sample onto it. A bluish discoloration indicates the presence of chlorine. If present then see Section 5.3 Interferences before proceeding with the distillation.

5.2 Pretreatment for Cyanides Amenable to Chlorination

Two sample aliquots are required for chlorine amenable cyanide determination. One is pretreated, the other is not pretreated. Both are prepped and analyzed and the difference between the two is the cyanide amenable to chlorination.

1.) To the sample aliquot designated for pretreatment add bleach solution dropwise until an excess of chlorine is maintained. Test for residual chlorine with KI-starch paper. Paper will turn blue.

2.) Maintain excess for one hour with continued agitation using a Teflon stir bar and a stir plate.

3.) After one hour, add ascorbic acid in small increments (~0.01 g) until KI-starch paper shows no residual chlorine and analyze.

5.3 Manual Distillation

Samples are distilled using the MIDI distillation method. The distillation procedure is as follows:

1) Remove fritted tubes from absorbers, rinse, and set aside.

2) Rinse out absorbers, and invert to drain.

3) Add 50.0 mL of a liquid sample (or 1.0 g of a solid sample) to a sample tube. For solid samples, dilute with DIW to the 50 mL mark on the tube.

4) Set up sample tubes for the appropriate QC (BS, PB, MS/MSD), but do not spike the BS or the "spiked" sample yet.

5) Add 3-4 boiling stones to each tube.

6) Insert reflux impingers into the sample tubes.

7) Fill the absorber tubes with 50.0 mL of 0.25 N NaOH, and insert the fritted tubes.

8) Place sample tubes in the back row of the heating block, and the absorbers into the front row.

9) Insert the cold-finger condensers into the top of the sample tubes.

10) Hook up all vacuum hoses.

11) Turn on water flow, and adjust flow meter to approx. the same number of samples that are being distilled (about 9-10 for 10 samples).

12) Plug in the vacuum pump.

13) Stabilize the flow rate at about 3 bubbles per second and wait for about 5 minutes.

14) Spike the BS and the MS/MSD with the appropriate spiking material.

15) Add 5 mL of 1:1 H_2SO_4 to each tube, and let mix for about 3 minutes.

16) Add 2 mL $MgCl_2$ to each tube, and rinse tubes with DIW.

17) Turn power on, and turn knob to mark.

18) When distillation is complete (10 minutes to heat to reflux, 60 mins of reflux, and 15 minutes of cooling) the heating block will automatically shut itself off. Replace tubes in tube rack, removing the fritted tubes before turning the vacuum pump off.

19) Pour off the liquid from the absorbers into a clean container, label, and store at 4°C if the distillates will not be analyzed immediately.

20) Rinse all glassware with DIW, and store fritted tubes in DIW.

5.4 Interferences

1.) Sulfide interference: Some sulfides convert CN^- to SCN^-. Add cadmium carbonate to sample until lead acetate test paper no longer darkens (treat 25 mL more than is necessary for the distillation). Yellow cadmium sulfide precipitates if the sample contains sulfide. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. Filter sample through a dry filter paper into a dry container then proceed with the distillation procedure. A narration is included in the final report. Run a standard or BS treated in the same manner with the treated samples.

2.) Chlorine interference: Chlorine decomposes most cyanides. Add ascorbic acid to the 50 mL sample ~0.02 g at a time until KI-starch test paper no longer turns bluish then add an additional 0.02 g of ascorbic acid. Proceed with the distillation procedure. A narration is included in the final report.

3.) NO_3 / NO_2 interference: Nitrates and/or nitrites can form oximes with organic compounds which can decompose under test conditions to form HCN. If high levels are suspected (e.g. fertilizers) then sulfamic acid is added to the sample to remove the interference.

4.) Surfactants. For manual distillation, the presence of surfactants may cause the sample to foam during refluxing. If this occurs, add an antifoam agent such as Baker Antifoam B Silicone Emulsion.

5.) Interferences are eliminated or reduced by the distillation procedure

6. Sample Analysis Using a Technicon Auto Analyzer

6.1 Instrument start-up and operation

The auto-analyzer should be set up for cyanide analysis according to the Laucks SOP on configuring the Technicon Autoanalyzer. Turn on power and allow heating bath to reach 150 degrees C while flushing reagent tubes with DIW. After the temperature is reached, place the reagent tubes into their proper reagents. Turn on chart drive motor and allow reagents to flow through completely. When baseline has settled, set baseline at about 90%T.

6.2 Analysis procedure

1) Prepare the 1.0 ppm working standard and the blank solution

2) From these solutions make the standard curve in 1 oz plastic cups, swirl and transfer to sampler cups, and load onto sampler.

3) Immediately after the calibration standards, load an EPA approved LCSW as the ICV. Immediately after the ICV, load the blank solution for the ICB.

4) Load standards, water samples, and distillates from manual distillation (distillates are analyzed the same as water samples) as in the following example and press the reset button on the autosampler to begin the analysis:

cup#	cup contains
1	STD 1 0 ppb
2	STD 2 10 ppb
3	STD 3 20 ppb
4	STD 4 50 ppb
5	STD 5 100 ppb
6	STD 6 150 ppb
7	STD 7 200 ppb
8	ICV/LCSW1
9	ICB
10	PBW1
11	Sample 1
12	Sample 1MS
13	Sample 1MSD
14	Next Sample
15	. . .
16	CCVx
17	CCBx

After sampling is finished and the last sample peak has been recorded, turn off the chart drive motor, put reagent tubes into wash and turn off the oil bath heater. Once the oil bath has cooled below 100 degrees C, the instrument can be entirely shut down.

6.3 Compound Quantification

The data for each sample is recorded in strip-chart form. On a bench sheet is recorded the information for each sample such as Sample ID, Cup #, and Dilution. Then the value for the Peak Ht and Baseline, as read from the strip-chart (to the nearest 0.25 units), is recorded for each sample. This data is then entered into a standard spreadsheet for the calculation of all other values. (An example of the spreadsheet is included in appendix II.)

- Percent transmittance is calculated from the formula: %T = Peak Ht/(Baseline/100) where the ratio Baseline/100 accounts for baseline drift.
- Absorbance is calculated from %T by the formula: Abs = 2-log(%T)
- The spreadsheet performs a linear regression including the calibration standards 0 mg/L up to 0.200 mg/L with x being the true value of the standards, and y being their corresponding absorbances.

- Concentration of CN^- in the samples is calculated from the linear regression curve using the formula y=mx+b. Substituting the sample absorbance as the y value and solving for x (conc. of CN^- in the same units as the standards were entered) and multiplying by the dilution factor, the formula becomes:

  conc. of CN^- = [(Abs. - y intercept) / slope] * dilution

7. Reports

7.1 Data Qualifying Flags

Sample report results are qualified with data qualifying flags. These flags have the following definitions:

CODE	Definition
U	: The analyte of interest was not detected, to the reporting limit.
*	: QC limits were exceeded.

Appendix I
Laucks Testing Laboratories
Method LTL 9104 QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	7 standards plus a blank. r ≥0.995	7 stds plus a blank, one std distilled as the BS. r ≥0.995	Beginning of run	Recalibrate if r < 0.995	In raw data.
Initial Calibration Verification / LCSW	Verify calibration every 15 samples with an independently prepared check standard.±15%.	Independent source ±15%.	1 per batch or 5% including one immediately after calibration.	Recalibrate	Enter in QC database under SRM.
Initial Calibration Blank	No criteria.	≤0.010 mg/L	1 per run immediately after ICV.	Recalibrate	In raw data.
Continuing Calibration Verification	Verify calibration with the mid-range standard. Must agree within 15% of true value.	Verify calibration with the mid-range standard. Must agree within 15% of true value.	1 after every 10 samples, and at the end of the run.	Perform instrument maintenance and recalibrate.	In raw data.
Continuing Calibration Blank	No criteria.	≤0.010 mg/L or reporting limit	1 after every 10 samples, and at the end of the run.	Check for source of contamination. Reanalyze associated samples.	In raw data.
Preparation Blank Soil: Water:	No criteria. No criteria.	≤0.50 mg/kg DB ≤0.010 mg/L or reporting limit	1 per batch or 5%.	Check for source of contamination. Reanalyze / reprep w/ associated samples.	Enter in QC database under BLANKS.
Matrix Spike (%Rec) Soil: Water:	Run one spike duplicate every 10 samples. No recovery criteria .	Refer to current control limits catalog	1 per batch or 5%	Spike at higher level or choose another sample and reanalyze / reprep w/ associated samples.	Enter in QC database under MSPKDATA.
Matrix Spike Dup. (RPD) Soil: Water:	See MS.	Refer to current control limits catalog	1 per batch or 5%	Same as MS.	Same as MS.
Blank Spike (%Rec) (Manually distilled soils and waters only.)	Two stds distilled and compared to equal values in standard curve.	Refer to current control limits catalog	1 per batch or 5%	Reprep w/ associated samples.	Enter in QC database under BS_CALC.

Appendix II

Excel spreadsheet used for cyanide calculations.
(example)

Cyanide Analysis	ITEM	DATE	METHOD	ANALYST	CHECKER	
JOB#:	prep.		Man. Distill	PL		
MATRIX: water	analysis	1/25/96	EPA 335.3	PL		

STANDARD CURVE LCSW: WP586 (tv=0.500 ppm)

standard stock:
TE4-67-17

T.V. (mg/L CN)	Peak Ht.	Baseline	%T	Absorbance
0.000	94.00	94.50	99.47	0.002
0.010	88.50	94.50	93.65	0.028
0.020	80.50	94.50	83.44	0.055
0.050	67.50	94.50	71.43	0.146
0.100	47.50	94.50	50.26	0.299
0.150	30.50	94.50	36.24	0.512
0.200	17.75	94.50	18.78	0.726
--x value--				--y value--

r = 0.9999 m = 2.9043 y(0) = 0.0022 x(0) = -0.0008

ms/msd=0.100ppm

Sample I.D.	Dilution	Peak Ht.	Baseline	%T	Absorbance	CN (mg/L)	
ICV / LCSW1	5	54.25	95.00	57.11	0.243	0.4151	83% Rec.
ICB	1	94.25	95.00	99.21	0.003	0.0004	ND
MDL tv=0.005	1	91.25	95.00	96.05	0.017	0.0053	105% Rec.
PBW1	1	94.50	95.00	99.47	0.002	0.0000	ND
5555-1	1	94.50	95.00	99.47	0.002	0.0000	ND
5555-1ms	1	48.00	95.00	50.53	0.296	0.1013	101% Rec.
5555-1msd	1	48.25	95.00	50.79	0.294	0.1005	101% Rec.
5555-2	1	94.25	95.00	99.21	0.003	0.0004	ND
5555-3	1	92.00	95.00	96.84	0.014	0.0040	ND
5555-4	1	89.00	95.00	93.68	0.028	0.0090	0.009
5555-5	1	88.50	95.00	93.16	0.031	0.0098	0.010
5555-6	1	65.75	95.00	69.21	0.160	0.0543	0.054
CCV1 tv=0.100	1	45.50	95.00	47.89	0.320	0.1093	109% Rec.
	1	94.00	95.00	98.95	0.005	0.0008	ND

Appendix III

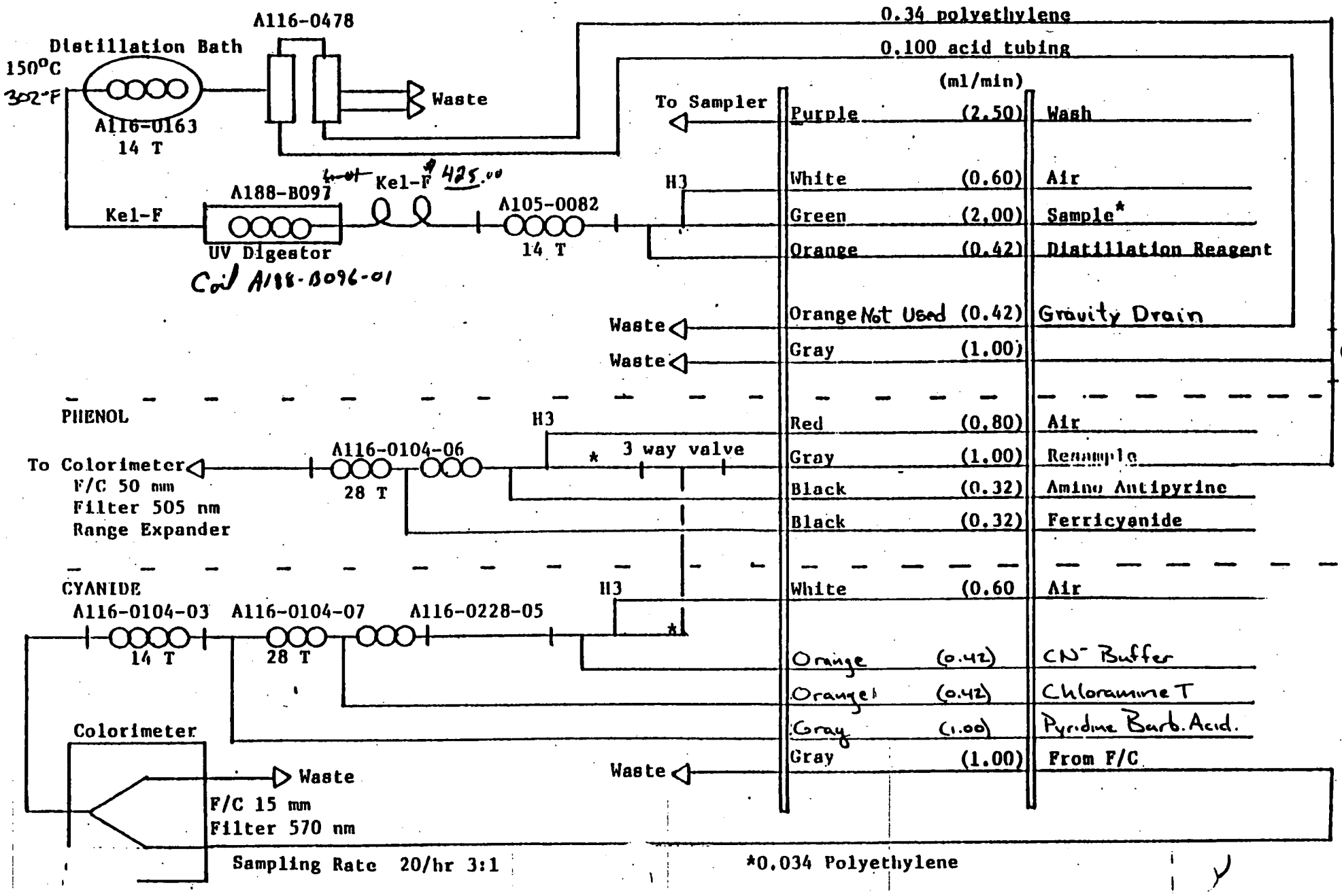
Autoanalyzer Flow Diagram

[illegible] Schematic
currently in use.
Jan 29, 1981 MS

CYAN[illegible]-PHENOL
Comb[illegible] Manifold
AAI

ALPKEN Co[illegible]ration
1981
RRP

DISTILLATION



LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #: LTL-9113

Title: **pH in Soil and Waste Samples Using SW846 Method 9045C**

Revision history:

Number	Date
1.0	07/13/94
2.0	01/16/97

UNCONTROLLED

Written by: Bill Lundberg Date: 1/16/97
Bill Lundberg, Inorganic Supervisor

Reviewed by: Harry Romberg Date: 1-16-97
Harry Romberg, QA Officer

Approved by: Karen J Kotz Date: 1/16/97
Karen Kotz, Lab Director

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method is an electrometric procedure for the determination of pH in soils and waste samples.

1.1.2 The sample is mixed with deionized water (DIW). The pH of the solution is then measured with a pH meter.

1.1.3 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Interferences:

1.2.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, which is not uncommon for some ash and other waste materials, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true value of <1, an uncommon condition, may give incorrectly high measurements.

1.2.2 Temperature fluctuations will cause measurement errors. Most pH electrodes are calibrated to 25°C. Whereas Laucks does use a temperature correction probe with the pH meter, significant differences in pH can affect the solubility and apparent pH characteristics of the solution itself. Therefore, measurements should be made near the appropriate temperature by allowing the sample and diluent (DIW) to warm to room temperature prior to analysis.

1.2.3 Errors can occur when the pH electrode becomes coated. If this occurs, the electrode must be thoroughly clean and re-buffered prior to measuring the pH of subsequent samples.

1.3 Sample Collection, Sample Storage, Holding Times

1.3.1 There is no official holding time for the analysis of soil pH. The holding time for aqueous samples is to analyze immediately. Soil should not demonstrate significant pH fluctuations if refrigerated and analyzed within a reasonable time but Laucks has chosen to analyze soils samples as soon as is reasonable after collection, not to exceed 7 days from collection.

1.4 Definition of Terms

1.4.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

1.4.1.1 **DIW** - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

1.4.1.2 **Sequence** - A set of sample extracts and standard solutions presented to an instrument in a chronologically continuous group.

2. Equipment List, Reagents and Standards

2.1 Apparatus

pH meter with means for temperature correction (temperature correction probe)
Glass electrode
50 ml. beaker
Analytical balance capable of weighing to 0.1 g.

2.2 Standards

pH 4 buffer
pH 7 buffer
pH 10 buffer

2.3 Reagents

Deionized water (DIW)

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Electrical shock - All instruments present the possibility of electrical shock The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.2 Waste Disposal

3.2.1 There should be no significant waste associated with this procedure which cannot be disposed of in the laboratory sink and/or garbage.

4. Calibration and Quality Control

4.1 Calibration

4.1.1 The pH meter must be calibrated with at least two pH buffers. One is the pH 7 buffer and the other depends upon the samples. If high pH is expected, the second buffer should be at pH 10 or higher. If low pH is expected, the second buffer should be the pH 4 buffer. High pH samples should not be analyzed from a low pH calibration and visa versa.

4.2 Sample Duplicate

4.2.1 Criteria

4.2.1.1 At least one duplicate sample per 10 samples per matrix is required. RPD values are not currently calculated for this analysis. The control limit is considered to be 0.5 pH units.

4.2.2 Corrective action

4.2.2.1 If an out-of-control duplicate pair is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation procedures

5.1 Sample preparation and pH measurement of soils

5.1.1 To 20 grams of soil in a 50 ml beaker, add 20 mls of DIW and stir the suspension for 5 minutes. This may also be done with a magnetic stirring bar.

5.1.2 Allow the suspension to stand for about 1 additional hour with no agitation in order to allow most of the suspended particulates to settle out.

5.1.3 Immerse the electrode (including the temperature correction probe) just far enough into the solution to establish good electrical contact. It should not come into contact with the soil itself.

5.1.4 The electrodes should be thoroughly rinsed between samples.

5.1.5 Report the results as "soil pH measured in water @ ____ °C."

5.2 Sample preparation and pH measurement of waste material:

5.2.1 To 20 grams of waste material in a 50 ml beaker, add 20 mls of DIW and stir the suspension for 5 minutes. This may also be done with a magnetic stirring bar.

5.2.2 Allow the suspension to stand for about 15 additional minutes with no agitation in order to allow most of the suspended particulates to settle out.

> Note: If the waste is hygroscopic and absorbs all the DIW, begin the test again using 20 g of waste and 40 ml of DIW.
>
> Note: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase.

5.2.3 Immerse the electrode (including the temperature correction probe) just far enough into the solution to establish good electrical contact. It should not come into contact with the waste material itself.

5.2.4 The electrodes should be thoroughly rinsed between samples.

5.2.5 Report the results as "waste pH measured in water @ _____ °C.

6. Reports

6.1 Data Packet Organization

6.1.1 The data package for this analysis consists of the data sheet and a quality control database (QC_DB) report form.

6.2 Quality Control Reports

6.2.1 All results for quality control tests are entered into the lab data base using the QC_DB program. The report form must be filled out in order to indicate that the duplicate QC had been performed and met the criteria specified in this document.

Appendix I

QC Summary Table

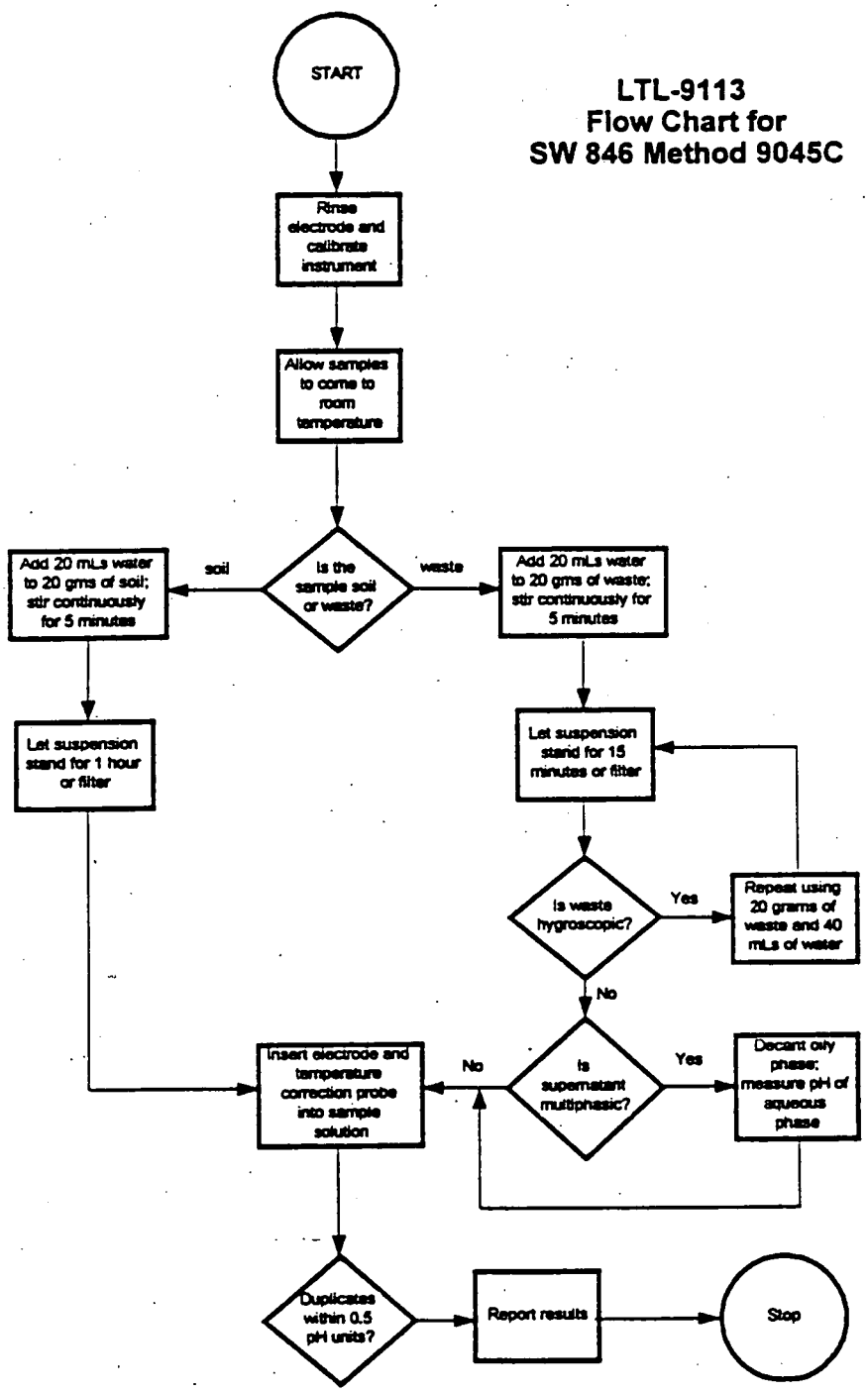
Laucks Testing Laboratories

Method SW 9045C QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	Buffer pH meter to bracket sample values	Buffer pH meter between pH 7 & 4 or 10 before analyses (to bracket sample values)	Once before analyzing any samples or QC	None	None
Duplicate % Difference	N/A	within 0.5 pH units of one another	10% or once every 10 samples.	Correct problem Consult QC Officer	QC_DB report form with appropriate commentary

Appendix II

Flow Chart


LTL-9113
Flow Chart for
SW 846 Method 9045C
START
Rinse electrode and calibrate instrument
Allow samples to come to room temperature
Is the sample soil or waste?
soil
waste
Add 20 mLs water to 20 grms of soil; stir continuously for 5 minutes
Add 20 mLs water to 20 grms of waste; stir continuously for 5 minutes
Let suspension stand for 1 hour or filter
Let suspension stand for 15 minutes or filter
Is waste hygroscopic?
Yes
Repeat using 20 grams of waste and 40 mLs of water
No
Is supernatant multiphasic?
No
Yes
Decant oily phase; measure pH of aqueous phase
Insert electrode and temperature correction probe into sample solution
Duplicates within 0.5 pH units?
Report results
Stop

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-9115

Title: **The Determination of Total Organic Carbon in Water Samples by SW846 9060.**

Revision history:

Number	Date
2	01/19/98
1.0	2/22/95

UNCONTROLLED

Written by: Bill Lundberg Date: 1/29/98
Bill Lundberg, Inorganics Supervisor

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Harry Romberg, QA Officer

Approved by: Karen J. Kotz Date: 1/29/98
Karen Kotz, Laboratory Director

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1. Introduction and Scope

1.1 Method Description

1.1.1 This method is used to determine the concentration of total organic carbon (TOC) in a water sample. The purgeable organic carbon (POC) is measured by sparging the acidified sample with oxygen for 3-5 minutes. The evolved gas is passed through a LiOH column to remove carbon dioxide formed from inorganic carbon (carbonates), combusted in a 950°C furnace, and measured using an IR detector. A system blank is subtracted from all POC readings before calculations are performed, this is to correct for any volatile carbon that may be present in the air at the time of analysis. Non-purgeable organic carbon (NPOC) is measured by injecting sparged, acidified sample into a chamber where a UV persulfate oxidation is performed. Carbon dioxide is evolved and measured in an IR detector. TOC is obtained by adding the POC and NPOC.

1.1.2 Method SW846 9060 states that all TOC analyses should be performed in quadruplicate. Laucks performs all TOCs in singlets, unless previous arrangements have been made with the client.

1.1.3 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter-type syringe. The openings of the syringe limit the maximum particle size which may be included in the sample..

1.1.4 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1 It is s rongly recommended that samples be collected in glass containers preserved with 0.2% sulfuric acid. Samples collected in plastic run the potential risks of: A) an increased TOC value due to organic carbon leaching from the plastic into the sample and/or B) a decreased TOC value due to solvents in the sample becoming incorporated into the plastic container.

1.2.2 In accordance with SW846 plastic containers are permissible. Laucks will however make every effort to provide glass containers.

1.2.3 Upon receipt samples should be stored at 4 ± 2°C.

1.2.4 The maximum recommended holding time for waters is 28 days from the date of sample collection. If this holding time is exceeded, the analyst should notify the project manager so that they may inform the client.

1.3 Definition of Terms

1.3.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

1.3.2 Batch Identifier - A number given to each preparation or analysis group which uniquely identifies that batch. This number is generally an analysis number which is similar to the blank ID, only preceded by an "A" rather than a "B" for inorganic batches. The preparation batch IDs are discussed in other documentation. The batch identifier for the second set of TOC in water analyzed on January 19,1998 would be A011998TOCW02

1.3.3 Blank spike - A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts of target analytes are added each time samples are prepared. Blank spikes are required on all HAZWRAP and NFESC work. Note that an LCS or SRM (see below) will substitute as a blank spike for most inorganic analyses. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard.

1.3.4 CCB - Continuing Calibration Blank - This is the same acronym used in the CLP program. This is a blank which is analyzed immediately after the CCV (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has maintained a stable baseline.

1.3.5 CCV - Continuing calibration verification. - This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has remained in calibration.

1.3.6 CLP - Contract Laboratory Program - The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.

1.3.7 DIW - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

1.3.8 ICB - Initial calibration blank - This term is borrowed from CLP. An instrument blank is made up in the same way as calibration standards, without target analytes.

1.3.9 ICV - Initial calibration verification - This term is borrowed from the CLP protocol. It is a standard which is analyzed at the start of each analytical run that is compared to the initial multi-point calibration to determine whether the instrument calibration is accurate. For most inorganic methods, this verification standard is from a source different from that used to make the calibration standards.

1.3.10 MDL - Method detection limit - The lowest concentration a sample which will yield a positive result that is greater zero at a known level of confidence. MDLs are empirically determined by Laucks.

1.3.11 SRM or LCS - Standard Reference Material or Laboratory Control Sample. This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This sample is used to demonstrate that the analytical system is in control..

1.3.12 QC period - Quality control period - An analysis sequence initiated by the analysis of one or more standards, followed by samples, and terminated with a standard and blank analysis. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP

1.3.13 RSD or %RSD - Relative standard deviation or percent relative standard deviation - The ratio of the standard deviation of a set of values to the mean of the set of values. A measure of the similarity of the values one to another.

1.3.14 Sequence - A set of sample extracts and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.

2. Equipment List and Standards

2.1 Instrument

2.1.1 TOC analyzer, Dohrman DC-80 or equivalent with POC furnace

2.1.2 Series of Unimetrics microliter syringes (1000, 200, and 40) or equivalent

2.2 Analytical balance: 0.1 mg sensitivity

2.3 Blender, Waring type, or equivalent.

2.4 Standards

2.4.1 NPOC potassium hydrogen phthalate (KHP) standards

2.4.1.1 Prepare a 4000 mg/l stock standard by dissolving 1700 mg ± 1 mg KHP in a 200 mL volumetric flask, dilute to the mark with DIW.

2.4.1.2 Prepare a 2000 mg/L intermediate standard by pipeting 50 ml of 4000 mg/L stock into a 100 ml volumetric flask, dilute to the mark with DIW.

2.4.1.3 Prepare 20 mg/L calibration standard by pipeting one ml of 2000 mg/L intermediate standard into a 100 ml volumetric flask, dilute to the mark with DIW

2.4.1.4 The 20 mg/l standard is prepared before each run. The 4000 and 2000 mg/l standards are to be made up monthly.

2.4.2 Preparation of POC Benzene standard

2.4.2.1 Prepare a stock solution of benzene in tetraglyme by adding about 25 ml of tetraglyme to a 50 ml volumetric flask. This should be done with a funnel in order to keep the neck of the flask dry. Cap the volumetric flask and weigh. Using a 5 ml glass syringe, draw up about 3 ml of benzene. Discharge the contents of the syringe into the volumetric flask just above the surface of the tetraglyme. Replace the cap and reweigh the flask. Fill to the mark with tetraglyme and mix well.

2.4.2.2 Calculate the concentration of the stock solution as follows:

$$\frac{\text{weight (mg) benzene}}{0.05} \times 0.923 = \text{mg/L C}$$

2.4.2.3 Prepare a POC intermediate standard by pipeting two mls of the stock solution into a 100 ml volumetric flask, dilute to mark with tetraglyme.

2.4.2.4 Prepare a working standard by filling a 100 ml volumetric flask to within 5 ml of the mark with DIW. Add 100 µl H_2SO_4, 100 µl antifoam, and one ml POC intermediate standard. Dilute to the mark with DIW. The working standard will be about 10 mg/L POC.

2.4.3 Preparation of glucose ICV solution

2.4.3.1 Prepare a 1000 mg/L stock solution by dissolving 250 mg ± 1 mg glucose in a 100 ml volumetric flask, dilute to the mark with DIW.

2.4.3.2 Prepare a 10 mg/L ICV solution by pipeting 1 ml of stock solution into a 100 ml volumetric flask, dilute to the mark with DIW.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.4 Electrical shock - All instruments present the possibility of electrical shock The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.5 Breathing protection and gloves should be worn when handling benzene.

3.1.6 The combustion furnace is heated to approximately 950°C, care should be taken when working in proximity of the furnace.

3.1.7 Care should be taken when handling persulfate reagent due to the high Hg content and strong oxidizing capabilities.

3.2 Waste Disposal

3.2.1 All waste generated during this analysis is collected in plastic jugs. These are then collected by a waste recycling firm.

3.2.2 Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

4. Calibration and Quality Control

4.1 Method Detection Limit Study

4.1.1 Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in Laucks on MDL studies. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration at 2-5 times the anticipated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL.

4.2 Initial Multi-Point Calibration

4.2.1 Analyze standard solutions using at least 3 different concentration levels. A 500ul injection ot the 20 mg/L standard is used to set the instrument's calibration, and a 1000ul injection of the 20 mg/L standard is used to define the upper range of useable data. A 250ul aliquot is used to demonstrate linearity.

4.2.2 Criteria

4.2.2.1 The correlation coefficient of the three points must be greater than .995.

4.2.3 Corrective action

4.2.3.1 If the criteria are not met, the instrument must be recalibrated.

4.3 Initial Calibration Verification

4.3.1 Immediately after the calibration curve, analyze a standard from a source other than that from which the calibration material was obtained.

4.3.2 Criteria

4.3.2.1 The calculated concentration of the ICV must be within the limits supplied by the manufacturer or should not exceed 90%-110% of the true value if no limits are provided.

4.3.3 Corrective action

4.3.3.1 If the ICV criteria are not met, no samples can be analyzed. Perform system maintenance and re-check the ICV. If the criteria still cannot be met, the system must be recalibrated.

4.4 Initial Calibration Blank

4.4.1 After the analysis of the ICV standard an instrument blank (ICB) is analyzed. The levels of target analytes in the CCB should not exceed the reporting limit.

4.4.2 Corrective action

4.4.2.1 If the initial CCB contains target analyte levels above twice the reporting limit, the system is out of control. The source of contamination must be identified and corrected before proceeding with the analysis.

4.5 Continuing Calibration Verification (CCV) and Blank (CCB)

4.5.1 A mid-range calibration standard is analyzed after every 10 samples. Immediately following the CCV, a blank solution is analyzed. In addition, this standard and blank must be the last samples analyzed in the run.

4.5.1.1 The CCV must fall within ± 10% of the true value.

4.5.1.2 The levels of target analytes in the CCB should not exceed twice the reporting limit.

4.5.2 Corrective action

4.5.2.1 If CCV limits are exceeded, check calculations or perform instrument maintenance. Recalibrate and reanalyze. No sample results may be reported that are not bracketed by a successful calibration and a CCV which is in control or by preceding and following CCVs which are within limits.

4.5.2.2 If the initial CCB contains target analyte levels above twice the reporting limit, the system is out of control. The source of contamination must be identified and corrected and the affected samples re-analyzed. As with the CCVs, no sample results may be reported that are not bracketed by a successful initial and continuing calibration blank which are in control or by preceding and following CCBs which are within limits.

4.6 Matrix Spike

4.6.1 A sample is chosen at random from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to preparation. The analyst should attempt to avoid selecting samples which are identified by the client as blanks. As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may also avoid selecting the most difficult sample of the batch for spiking. It is not always required that a matrix spike analysis be performed with each preparation/analysis batch, however, the minimum frequency for MS analysis is 1 each per 10 samples per matrix. This will be best accomplished by running one with every batch for many analyses. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$\text{recovery} = \frac{(SS - S) * 100}{SA}$$

where:

SS = concentration in spiked sample
S = native concentration in unspiked sample
SA = spiked added, the amount of spiking material actually added to the sample calculated on the sample basis

4.6.2 The recovery criteria are detailed in the Quality Control Database (QC_DB) and will change from time to time.

4.6.3 Corrective action

4.6.3.1 Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action will first involve recalculation, followed by possible re-preparation, and/or reanalysis. This process should also look at the recovery of at the recovery of matrix spiking compounds from the SRM and/or blank spike analysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.7 Matrix Spike Duplicate

4.7.1 The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values. This calculation is as follows:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where:
S1 = measured concentration for MS sample
S2 = measured concentration for MSD sample

RPD control limits are detailed in the Quality Control Database (QC_DB) and will change from time to time.

4.8 Sample Replicates

4.8.1 Criteria

4.8.1.1 The method requires that all samples be analyzed in quadruplicate. It then requires that the mean and the range be reported. Some clients may chose to have their samples analyzed at a lower frequency. If this is the case, then samples will be analyzed in duplicate with a minimum frequency of 1/20.. RPD values are calculated in a manner similar to MS/MSD RPDs:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where:
S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analysis

4.8.1.2 The RPD control limits are detailed in the Quality Control Database (QC_DB) and will change from time to time.

4.8.2 Corrective action

4.8.2.1 If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation procedures

5.1 Sample Analysis

5.1.1 Sample prep

5.1.2 Verify that the pH of the sample is <2.

5.1.3 If the sample contains a visible amount of suspended material, it should be homogenized by using the blender until it appears that all the sample reduction has taken place. If the sample still appears to be non-homogeneous, the analyst should disuss the situation with the project manager.

5.1.4 The POC portion of the analysis *must* be completed before homogenization, due to potential loss of volatile organic carbon.

5.1.5 Analysis sequence

NPOC Calibration standard (10 mg/L)
20 mg/L linearity check standard
5 mg/L linearity check standard
NPOC method blank
SRM
Matrix blank
POC method blank (3x)
System blank (3x)
POC standard
10 mg/L glucose ICV
ICB Blank (NPOC)
10 or fewer POC readings (may include QC)
10 mg/L NPOC standard (CCV)
Blank (NPOC, CCB)
Additional POC readings (10 maximum)

10 mg/L NPOC standard (CCV)
Blank (NPOC, CCB)

10 or fewer NPOC readings (may include QC)
10 mg/L NPOC standard (CCV)
Blank (NPOC, CCB)
Additional NPOC readings (10 maximum)
10 mg/L NPOC standard (CCV)
Blank (NPOC, CCB)

10 mg/L NPOC standard (CCV)
Blank (NPOC, CCB)

5.2 Instrumental Conditions

5.2.1 The instrument with POC furnace is assembled according to manufacturers instructions.

5.2.2 A gas flow of 200 ± 20 ml/min. oxygen is set for the furnace.

5.2.3 A reagent flow of 3.2 to 3.8 ml/min. is set for the recycle pump tube.

5.2.4 A reagent flow of 0.6 to 0.8 ml/min. is set for the fresh reagent pump tube.

5.3 Analytical Operation

5.3.1 Instrument startup

5.3.1.1 The furnace is turned on and allowed 90 min. to stabilize.

5.3.1.2 The reactor vessel is filled with reagent, pump and UV lamp are turned on, and the vessel is given at least 30 min. to stabilize.

5.3.1.3 Instrument is set for one ml sample size and for TOC mode.

5.3.1.4 When POC readings are being determined, the mode switch is set to POC.

5.3.2 POC determinations

5.3.2.1 POC readings must be made prior to NPOC reading due to potential loss of POC when opening the sample container.

5.3.2.2 With the instrument set to POC mode a one ml sample is injected into the POC sparger.

5.3.2.3 Push the start button, sample is sparged for 3.5 minutes, and the POC value is printed on the strip chart. If the value is higher than the highest standard, the sample must be diluted and reanalyzed

5.3.2.4 The determined system blank value is subtracted from the strip chart value before any calculations are done.

5.3.2.5 Proceed with the next POC reading or CCV.

5.3.3 NPOC determination

5.3.3.1 Sample is placed in a solo cup and sparged with the external sparger for 3.5 minutes.

5.3.3.2 With the instrument in TOC mode an appropriate amount of sample is injected into the instrument via the injection port, the NPOC value is then printed on the strip chart. If the value is higher than the highest standard, the sample must be diluted and reanalyzed

5.3.3.3 If NPOC is below one mg/L and less than one ml of sample was injected, rerun with a larger size aliquot.

5.3.3.4 If time out error occurs, wait for the detector to return to baseline and rerun sample using a smaller aliquot.

5.3.3.5 According to manufacturers instructions samples displaying a NPOC greater than 20 mg/L must be diluted and rerun. A 20 mg/L verification standard is run to demonstrate that the curve is linear to 20 mg/L.

5.4 Compound Quantification

5.4.1 TOC is determined by adding the POC and NPOC values together after they have been multiplied by their appropriate dilution factors.

6. Reports

6.1 Data Packet Organization

6.1.1 A data package will consist of the Excel spreadsheet used to quantify the TOC and a copy of the QC-DB report summary. If the client requests, the instrument output will also be provided.

6.2 Quality Control Reports

6.2.1 In addition to the sample results, all results for the quality control tests are entered into the lab data base using the QC_DB program. These results include those for the method blank analyses (both NPOC and POC method blanks are reported), matrix spike results, duplicate results, and standard reference material (SRM) reports. It is not necessary to include a copy of the information entered into the QC_DB program with each job. However, a copy of the QC_DB report form must be included in order to indicate that the QC was evaluated for analytical consistency.

6.3 Sample Result Reports

6.3.1 Data Qualifying Flags

6.3.1.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

CODE	Definition
U	: The analyte of interest was not detected, to the limit of detection indicated.

6.4 Control Chart(s)

6.4.1 The recovery values for the LCS/SRM are plotted on control charts which may also be supplied to clients upon request.

Appendix I

QC Summary Table

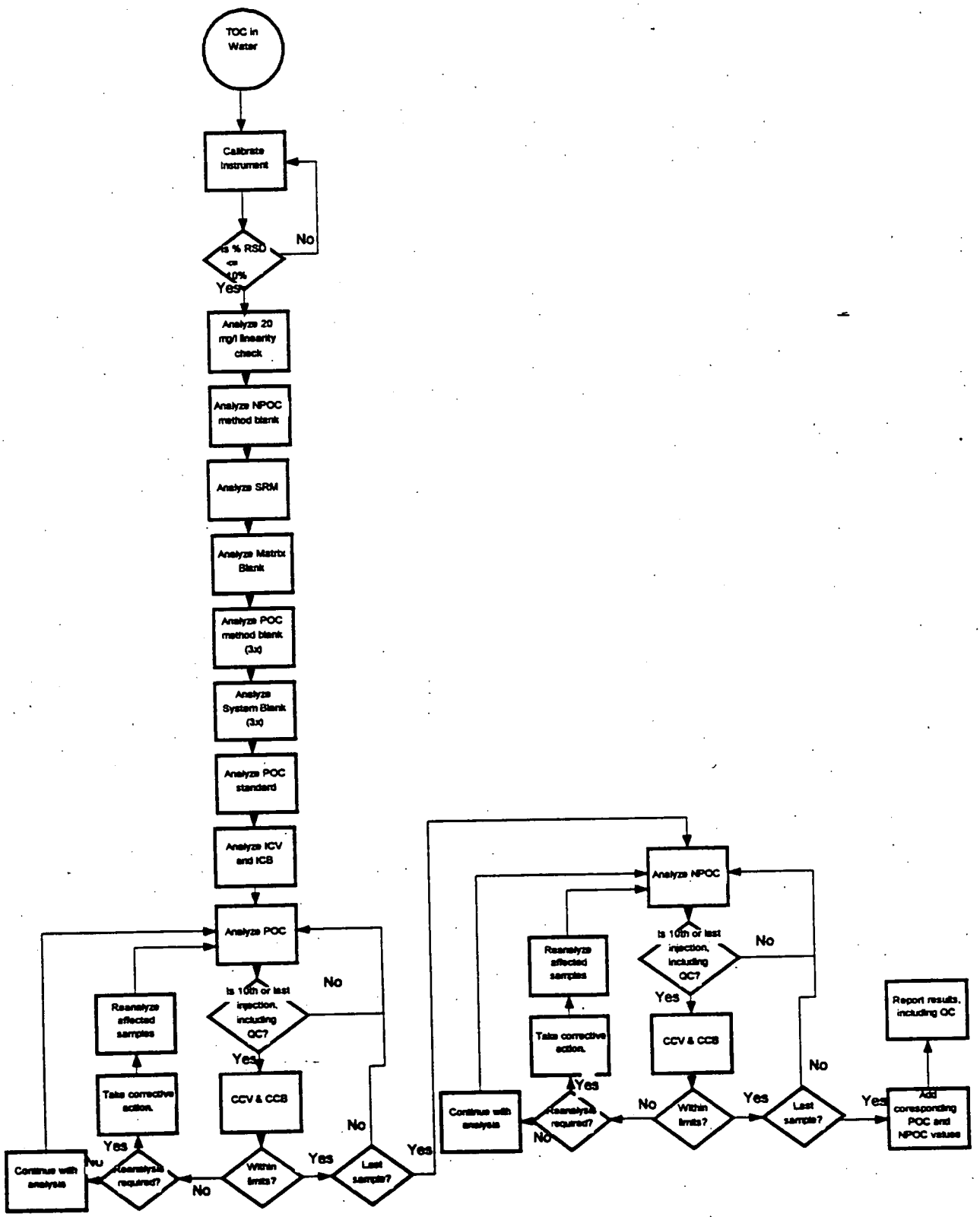
Laucks Testing Laboratories
Method _9060 QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	Per Manufacturers Instructions	Per Manufacturers Instructions. See SOP section 4.2.	Once per run	Fix problem and re-calibrate	In raw data package
Initial Calibration Verification	Verify with an independently prepared check standard. No limits stated.	Verified with 10 mg/l glucose standard. Limits ± 10% (9.0 - 11.0)	Once per run	Reanalyze, remake solution, and/or recalibrate	In raw data package
Initial Calibration Blank	N/A	Must be less than reporting limit	Run after ICV	Reanalyze	In raw data package
Continuing Calibration Verification	Every 15 samples with an independently prepared standard, no limits	Verify with 10 mg/L standard; CCV must be within 10% of true value	After every 10 injections and at the end of the run.	Fix problem and re-calibrate; re-analyze samples which are not bracketed by valid CCVs	In raw data package
Continuing Calibration Blank	N/A	Must be less than reporting limit	Run after each CCV	Reanalyze	In raw data package
Linearity Check Standard	N/A	Verify with 20 mg/L standard; must be within 10% of true value	Once after NPOC calibration standard	Reanalyze, remake and/or recalibrate instrument	In raw data package

POC standard	N/A	Must meet current spike recovery limits	Once after POC method and system blanks	Remake standard	In raw data package
Method Blank	Once per sample batch; must be less than MDL	Must be less than reporting limit	One POC and one NPOC per batch	Reanalyze	In raw data package
Matrix Spike Recovery	Once every 10 samples; no criteria	Refer to current QC limits catalog and/or QC database	One MS/MSD pair per run or per 20, which ever is greater	Review data; consult QC officer; some conditions may require re-analysis	Narrative comment in report and raw data package
MS/MSD RPD	N/A	Refer to current QC limits catalog and/or QC database	One MS/MSD pair per run or per 20, which ever is greater	Review data; consult QC officer; some conditions may require re-analysis	Narrative comment in report and raw data package
Duplicate % Difference	N/A	Refer to current QC limits catalog and/or QC database	Once every 20 samples	Review data; consult QC officer; some conditions may require re-analysis	Narrative comment in report and raw data package
Standard Reference Material (SRM) Recovery	N/A	Values are supplied by manufacturer	Once every 20 samples	Review data; consult QC officer	Narrative comment in report and raw data package

Appendix II

Flow Chart


TOC in Water
Calibrate Instrument
Is % RSD <= 10%
No
Yes
Analyze 20 mg/l linearity check
Analyze NPOC method blank
Analyze SRM
Analyze Matrix Blank
Analyze POC method blank (3x)
Analyze System Blank (3x)
Analyze POC standard
Analyze ICV and ICB
Analyze POC
Is 10th or last injection, including QC?
No
Yes
CCV & CCB
Within limits?
Yes
No
Last sample?
Yes
No
Reanalyze affected samples
Take corrective action.
Reanalysis required?
Yes
No
Continue with analysis
Analyze NPOC
Is 10th or last injection, including QC?
No
Yes
CCV & CCB
Within limits?
No
Yes
Last sample?
No
Yes
Reanalysis required?
Yes
No
Reanalyze affected samples
Take corrective action.
Continue with analysis
Report results, including QC
Add corresponding POC and NPOC values

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-9125

EPA 353.2 Nitrate/Nitrite as N by Lachat

Revision history:

Number	Date
0	04/23/96
1	10/28/98

UNCONTROLLED

Written by: Bill Lundberg, Inorg Div. Manager Date: 10/28/98

Approved by: Harry Romberg, QC Officer Date: 10-29-98

Approved by: Kathy Kreps, Laboratory Director Date: 10/28/98

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1. Introduction and Scope

1.1. Method Description

1.1.1. This method is applicable to the determination of nitrate/nitrite in drinking, surface and saline waters, domestic and industrial wastes. The method is applicable in the range from 0.010 to 2.00 mg/L as N. Higher nitrate/nitrite concentrations can be determined by diluting the sample. The nitrate in the sample is quantitatively reduced to nitrite by passing it over a cadmium reduction column. The diazonium compound formed by diazotation of sulfanilamide by nitrite in water under acid conditions is coupled with N-(1-napthyl)-ethylenediamine dihydrochloride to produce a reddish-purple color which is measured in a spectrophotometer at 520 nm.

1.1.2 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2. Sample Collection, Sample Storage, Holding Times

1.2.1. Samples are collected in plastic 500 mL bottles. They are preserved with H_2SO_4 to pH <2. The samples should be held at 4±2 C° until analysis. The holding time is 28 days, based on time of collection.

1.3. Definition of Terms

1.3.1. This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

1.3.2. **Batch Identifier** - A number given to each preparation or analysis group which uniquely identifies that batch. This number is an analysis number which is similar to the blank ID, only preceded by an "A" rather than a "B" for inorganic batches. The preparation batch IDs

are discussed in other documentation. The batch identifier for the third batch of waters run on Feb 29,1996 would be: A022996LANNW03

1.3.3. **Blank spike** - A background free matrix (DIW for water, clean sand for soils/sediments) to which known amounts of target analytes are added each time samples are prepared. Blank spikes are required on all HAZWRAP and NFESC work. Note that an LCS or SRM (see below) will substitute as a blank spike for most inorganic analyses. In the context of this SOP, a blank spike is the same as a QC check standard. See also QC check standard.

1.3.4. **CCB** - Continuing Calibration Blank - This is the same acronym used in the CLP program. This is a blank which is analyzed immediately after the CCV (almost always after every 10 samples and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has maintained a stable baseline.

1.3.5. **CCV** - Continuing calibration verification. - This is the same acronym used in the CLP program. This is a standard analyzed at some prescribed frequency (immediately following calibration, after every 10 samples, and at the end of the analytical run) during the analysis sequence to determine whether the instrument or system has remained in calibration.

1.3.6. **CLP** - Contract Laboratory Program - The USEPA program that contracts with laboratories to provide laboratory services. The term has come to mean a much broader set of methods and deliverables. In context of this SOP, CLP means procedures or operations which are detailed in the CLP contract and which are extended to a broader working definition.

1.3.7. **Corr Coef, CC** - Correlation coefficient - A measure of the "goodness of fit" of a set of data to a regression model. The closer the value is to 1, the higher the degree of confidence in the correlation

1.3.8. **DIW** - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

1.3.9. **ICB** - Initial calibration blank - This term is borrowed from CLP. An instrument blank is made up in the same way as calibration standards, without target analytes.

1.3.10. **ICV** - Initial calibration verification - This term is borrowed from the CLP protocol. It is a standard which is analyzed at the start of each analytical run that is compared to the initial multi-point calibration to determine whether the instrument calibration is accurate. For most inorganic methods, this verification standard is from a source different from that used to make the calibration standards.

1.3.11. **IDL** - Instrument detection limit. The lowest concentration of a target analyte that will yield a signal:noise ratio of least 3x. Used as a starting point for selecting MDL study spiking levels.

1.3.12. **MDL** - Method detection limit - The lowest concentration a sample which will yield a positive result that is greater zero at a known level of confidence. MDLs are empirically determined by Laucks.

1.3.13. **MDL standard** - Method detection limit standard - A standard prepared so that the concentrations of the target analytes are no greater than 4x the empirically determined MDLs. This standard is used to verify that the instrument or system is capable of detecting the target analytes on an ongoing basis.

1.3.14. **QC check standard** - Quality control check standard. Referred to in this SOP as a blank spike. A QC check standard is used to determine whether the analytical system is in control if MS/MSD recoveries are out of control. See also blank spike.

1.3.15. **SRM or LCS** - Standard Reference Material or Laboratory Control Sample. This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This sample is used to demonstrate that the analytical system is in control

1.3.16. **QC period** - Quality control period - An analysis sequence initiated by the analysis of one or more standards, followed by samples, and terminated with a standard and blank analysis. A QC period can be open-ended chronologically, but calibration verification must be documented using the procedures in this SOP

1.3.17. **RSD or %RSD** - Relative standard deviation or percent relative standard deviation - The ratio of the standard deviation of a set of values to the mean of the set of values. A measure of the similarity of the values one to another.

1.3.18. **Sequence** - A set of sample extracts and standard solutions injected into an instrument in a chronologically continuous group. See also QC period.

2. Equipment List and Standards

2.1. Instrument

2.1.1 Lachat QuickChem AE-200

2.1.2 Reaction Module 10-107-04-1-C

2.1.3 Cd/Cu column. This is purchased pre-packed from Lachat.

2.1.4 Autosampler

2.1.5 Proportioning Pump

2.1.6 IBM PC with software for capturing and reducing the data.

2.2. Standards

2.2.1. Stock Nitrate solution: A commercially prepared solution of 100 mg/L NO_3-N is purchased annually. This solution will be preserved with 0.2% $CHCl_3$

2.2.2 Intermediate Nitrate Standard: Dilute 2000 µLs of 2.2.1 to 100 mLs in a volumetric flask with 0.2 % H_2SO_4. The concentration of this solution is 2.0 mg/L. This solution should be prepared weekly.

2.2.3 Working standards: Dilute 0, 500µl, 1000µl, 5.0 mL, and 20.0 mL of 2.2.2 to 20 mLs with 0.2% H_2SO_4. The concentration of these solution are zero, .050 mg/L, .100 mg/L, .500 mg/L and 2.000 mg/L. These solutions should be made fresh daily. The CCV solution is the .500 mg/L standard. MS/MSD samples are prepared by diluting 25µl of 2.2.1 to 5.0 mLs with the sample. The MDL solution is prepared by diluting 25 µl of 2.2.2 into 5.0 mLs of 0.2 % H_2SO_4.

2.3 Reagents

2.3.1 Ammonium chloride buffer: Dissolve 85. g of NH_4Cl and 1.0 g EDTA in approx 900 mLs DIW. Adjust the pH to 8.5 with 15M NaOH. Dilute to 1L and mix.

2.3.2 Sulfanilamide color reagent: In a 1L volumetric flask, combine 600 mL of DIW, 100 mL of 85% H_3PO_4, 40.0 g of sulfanilamide, and 1.0 g N-1-napthylethylenediamine dihydrochloride. Stir for 20 mins, or until dissolved. Dilute to 1L and mix.

2.3.3 Carrier: Dilute 3 mL of conc. H_2SO_4 to 1.5 L with DIW.

3. Safety precautions and Waste Disposal

3.1. Safety Precautions

3.1.1. All standards, samples and sample solutions should be handled as if they are hazardous substances.

3.1.2. Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3. Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.4. Electrical shock - All instruments present the possibility of electrical shock The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.5 Sodium hydroxide and sulfuric acid are extreme irritants if they come in contact with skin or eyes. When using these chemicals, the analyst should wear gloves and safety glasses.

3.2. Waste Disposal

3.2.1. Waste from the instrument is carried by a drain to the sink. Leftover sample aliquots are also disposed of into the sink..

3.2.2. Waste segregation and disposal from the point of collection is further covered in the Laucks SOP on Waste Segregation and Disposal.

4. Calibration and Quality Control

4.1. *Method Detection Limit Study*

4.1.1. Prior to the analysis of any samples, it is necessary to establish method detection limits. This procedure is fully described in Laucks on MDL studies. Briefly, it involves the analysis of 7 replicate samples spiked at a concentration near the anticipated method detection limit. A Student's T-test is then applied to these measured values to calculate the MDL.

4.2. *Initial Multi-Point Calibration*

4.2.1. Analyze standard solutions using at least 4 different concentration levels. The calibration curve was described in the Standards section. The lowest standard is at .050 mg/L. The highest standard is 2.00 mg/L. The calibration solutions are analyzed from the highest concentration to the lowest

4.2.2. Criteria

4.2.3. Initial calibration data is evaluated using the correlation coefficient of a linear regression analysis. The correlation coefficient must be 0.995 or greater for a 5-point calibration. All CCVs and sample concentrations must be computed using the regression equation.

4.2.4. Corrective action

4.2.5. If the criteria are not met, the instrument must be recalibrated.

4.3. *Initial Calibration Verification*

4.3.1. Immediately after the calibration curve, analyze a standard from a source other than that from which the calibration material was obtained.

4.3.2. Criteria

4.3.3. The calculated concentration of the ICV must be within the limits supplied by the manufacturer or should not exceed 90%-110% of the true value if no limits are provided.

4.3.4. Corrective action

4.3.5. If the ICV criteria are not met, no samples can be analyzed. Perform system maintenance and re-check the ICV. If the criteria still cannot be met, the system must be recalibrated.

4.4. *Initial Calibration Blank*

4.4.1. After the analysis of the ICV standard an instrument blank (ICB) is analyzed. The absolute value of NO_2/NO_3 in the CCB should not exceed the reporting limit.

4.4.2. Corrective action

4.4.2. If the initial CCB contains target analyte levels above the reporting limit, the system is out of control. The source of contamination must be identified and corrected before proceeding with the analysis.

4.5. Method Detection Limit Standard

4.5.1. After the analysis of the ICV and the ICB, but before the analysis of any samples, an MDL standard is to be analyzed. The MDL standard is used to provide on-going verification of the ability of the system to detect analytes at a concentration near the method detection limit. The MDL standard should give a positive result. It must be detected for the system to be considered in control.

4.5.2. Corrective Action

4.5.3. If NO_2/NO_3 is not detected, the analysis must be terminated until the problem has been solved. Alternatively, if the affected samples are well above the detection limit (i.e. bracketed by appropriate standards), they may be reported. No undetected values should be reported if the MDL standard for that analyte(s) is undetected.

4.6. *Continuing Calibration Verification (CCV) and Blank (CCB)*

4.6.1. A mid-range calibration standard is analyzed after calibration and after every 10 samples. Immediately following the CCV, a blank solution is analyzed. In addition, this standard and blank must be the last samples analyzed in the run.

4.6.2. The CCV must fall within ± 10% of the true value.

4.6.3. The levels of NO_2/NO_3 in the CCB should not exceed the reporting limit.

4.6.4. Corrective action

4.6.5. If CCV limits are exceeded, check calculations or perform instrument maintenance. Recalibrate and reanalyze. No sample results may be reported that are not bracketed by a successful calibration and a CCV which is in control or by preceding and following CCVs which are within limits.

4.6.6. If the initial CCB contains target analyte levels above the detection limit, the system is out of control. The source of contamination must be identified and corrected and the affected

samples re-analyzed. As with the CCVs, no sample results may be reported that are not bracketed by a successful initial and continuing calibration blank which are in control or by preceding and following CCBs which are within limits.

4.7. *Method Blanks*

4.7.1. Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time or at least one blank every 20 samples which ever is more frequent. Any analyte response above the detection limit is reported. Method blank control limits are that contamination should not exceed the reporting limit

4.7.2. Corrective action

4.7.3 .Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if an analyte were found in the blank but not in any of the associated samples then sample group may not require re-analysis. In addition, if sample levels exceed 20 times the blank, the level of contamination may be considered insignificant. In any case, if re-preparation and re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Control Officer. It is the laboratory's responsibility to ensure that method interferences caused by contaminants in acids, solvents, reagents, glassware, and other sample processing hardware leading to discrete artifacts and/or elevated baselines in the analytical run be minimized. In the extreme case of chronic contamination, blanks may have to be analyzed from each stage of the sample processing to determine the contamination source so it can be eliminated. In all cases where blank contamination exceeds the control limit, a narrative comment must be made which documents the corrective actions taken.

4.8. *Matrix Spike*

4.8.1. A sample is chosen at random from the samples to be analyzed, and an aliquot of spiking solution is added to this sample prior to analysis such that the final solution is fortified at 0.500 mg/L. The analyst should attempt to avoid selecting samples which are identified by the client as blanks. As the purpose of the matrix spike is to test the system under "typical" conditions, the analyst may also avoid selecting the most difficult sample of the batch for spiking. It is always required that a matrix spike analysis be performed with each preparation/analysis batch, however, the minimum frequency for MS analysis is 1 each per 20 samples per matrix.. This matrix spike sample is used to evaluate the matrix effect of the sample upon recovery of the analytes. The recovery of spike analytes is calculated as follows:

$$\% \text{ recovery} = \frac{(SS - S) * 100}{SA}$$

where:

SS = concentration in spiked sample
S = native concentration in unspiked sample
SA = spike added, the amount of spiking material actually added to the sample calculated on the sample basis

4.8.2. The recovery criteria are detailed in the current Control Limits Catalog and in the Quality Control Database and will change from time to time.

4.8.3. Corrective action

4.8.4. Samples with spike recoveries outside control limits will be reviewed for possible corrective action. Corrective action will first involve recalculation, followed by possible re-preparation, and/or reanalysis. This process should also look at the recovery of the matrix spiking compounds from the SRM and/or blank spike analysis. If the SRM is in control, the out of control recovery is due to matrix interference and probably does not warrant reanalysis. In all cases a narrative explanation of the condition is required to detail the corrective actions taken.

4.9. *Matrix Spike Duplicate*

4.9.1. The compound recovery criteria are identical to those for the matrix spike sample. In addition, the matrix spike duplicate is used measure method precision. This is done by computing the relative percent difference (RPD) between the matrix spike and matrix spike duplicate recovery values. MS/MSD is the preferred method for measuring precision, however if the client requests, or if it is to reported in CLP format, MS/DUP is performed. This calculation is as follows:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where:

S1 = measured concentration for MS sample
S2 = measured concentration for MSD sample

4.9.2. RPD control limits are detailed in the current Control Limits Catalog and in the Quality Control Database (QC_DB) and will change from time to time.

4.10. *Sample Duplicate*

4.10.1. Criteria

4.10.2. Sample duplicates are required only when the client requests, when CLP practices are employed, or when the method specifically calls for duplicates. At least one duplicate sample per 20 samples per matrix is required when matrix spikes/duplicates are being performed. RPD values are calculated in a manner similar to MS/MSD RPDs:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where:
S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analysis

4.10.3. The RPD control limits are detailed in the current Control Limits Catalog and in the Quality Control Database and will change from time to time.

4.10.4. Corrective action

4.10.5. If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility. Generally, if recoveries are in control and no analyte of interest was detected in any of the samples, no immediate action will be taken on that sample set. If integrity of reported sample values is in doubt, re-analysis may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation procedures

5.1. Sample Analysis

5.1.1. Analysis sequence

S0
S1
S2
S3
S4
ICV
CCV0
ICB
MDL
PB
Sample A
Sample A Spike
Sample A Spike Dup (or Dup)
Sample B
etc.
after 10 samples
CCV1
CCB1

A CCV and CCB must be the last samples analyzed..

5.2. Instrumental Conditions

5.2.1. Proportioning pump set at 35.

5.2.2 Injection valve with 17 cm of 0.8 mm i.d. tubing.

5.2.3 Reaction Module 10-107-04-1-C

5.2.4 Colorimeter with 520 nm filter, and 10 mm flow cell.

5.3 Analytical Operation

5.3.1 Turn on the system at the power strip, and allow to warm up for 5-10 mins.

5.3.2 Download the method by selecting "NN" in the Analysis Select and Download screen.

5.3.3 Place reagent feed tubes into the proper containers.

5.3.4 Lock pump tube cassettes down on the pump, and raise the tension levers to vertical.

5.3.5 Pump reagents until all air is expelled from the tubing.

5.3.6 Stop the pump, place the cadmium column in line on the manifold, and restart the pump.

5.3.7 Make up the standards as described in the standards section.

5.3.8 Begin calibration by selecting " Calibrate Now" under the "Submit" menu. Follow instructions on the screen to begin calibration.

5.3.9 After calibration approval, verify that the correlation coefficient is >0.995.

5.3.10 Load samples into a tray and record their position in the "Identification" field of the "Submit" menu Record any dilutions made in the "Dilution" field.

5.3.11 Submit the tray by choosing "Submit Current Tray". Give the appropriate responses to the prompted fields.

5.3.12 After analysis is complete, move to the "Results/Approval" field. To print the report, choose Tray selection, Sample tray, Reports, Print reports.

5.3.13 After analysis is completed, stop pump, remove the Cadmium column, place the reagent tubes in DIW and pump for 5 mins to clean the system.

5.3.14 Remove the tubes from the DIW, pump air until all liquid is expelled, unlatch the pump tubes, and turn off the power strip.

5.4 Compound Quantification

5.4.1 The instrument report is in mg/L. This value is corrected for any dilution inputted into the software. Any external dilutions need to be corrected for on the report. Soil samples are reported in mg/Kg DB using the following equation:

$$\text{Nitrate/Nitrite, mg/Kg DB} = \frac{\text{N/N in extract* dilution}}{\text{\% TS/100}}$$

5.4.2 Any samples having concentrations above the high standard are diluted with 0.2% H_2SO_4 and reanalyzed.

6. Reports

6.1. Data Packet Organization

6.1.1. A data package will consist of a copy of the calibration, a copy of the quantitation report for the samples, a data summary showing any external calculations (i.e., TS corrections), and a QC summary report showing where the records are located in the QC data base. A CLP like package will also require a runlog showing all the standards preparation, standard and QC solution references, and the analytical sequence and it's timing.

6.2. Quality Control Reports

6.2.1. All results for quality control tests are entered into the lab data base. A report of all data entered must be included in the data packet. The routine minimum is a method blank report, and an MS/MSD or MS/duplicate report. Many analyses will also require an SRM, blank spike or other report.

6.3. Sample Result Reports

6.3.1. Data Qualifying Flags

6.3.1.1. Sample report results are qualified with data qualifying flags. These flags have the following definitions:

CODE	Definition
U	: The analyte of interest was not detected, to the limit of detection indicated.

6.4. Control Chart(s)

6.4.1. The recovery values for nitrate/nitrite in the SRM are plotted on control charts.

Appendix I

Laucks Testing Laboratories

Method 353.2 NO3/NO2

QA Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Initial Calibration	3 pt calibration	4 pt calibration R≥0.995	Daily	Recalibrate	Copy of calibration in package
Initial Calibration Verification	90-110%	90-110% or manufactures limits	1/20	Recalibrate	Included in raw data
Initial Calibration Blank	< MDL	Less than the reporting limit	Once per run	Reanalyze or recalibrate	Included in raw data
Continuing Calibration Verification	90-110%	90-110 %	Every 10 samples, after cal., and at the end	Recalibrate	Included in raw data
Continuing Calibration Blank	<MDL	Less than the reporting limit	Every 10 samples and at the end	Recalibrate	Included in raw data
MDL standard recovery	None required	Must be detectable	Once per run	Recalibrate	Included in raw data
Method Blank	1/ batch < MDL	Less than the reporting limit	One per 20	Reanalyze or recalibrate unless sample>20X MB	Included in raw data
Matrix Spike	10% frequency 90-110%	See QC database	* One per 20	Reanalyze	QC database
Matrix Spike Duplicate	None required	See QC database	* One per 20	Reanalyze	QC database

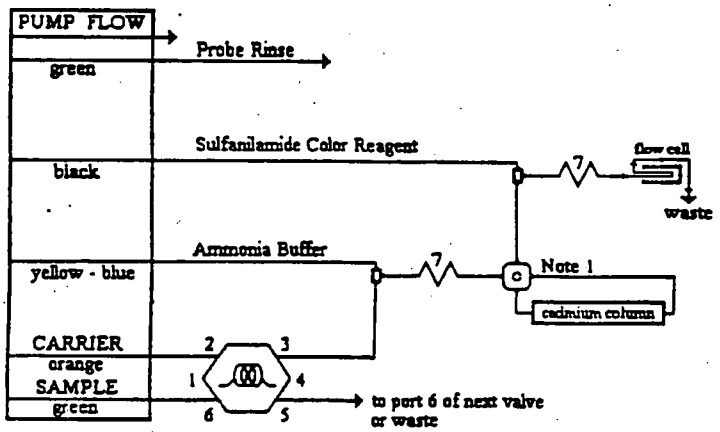
Duplicate % Difference	None required	See QC database	* One per 20	Reanalyze	QC database
Lab Fortified Blank	1/ batch 90-110%	This is the same as the ICV			

* Either a MS/MSD or a MS/DUP will be run with every batch

Appendix II

Manifold Schematic from Current Instrument Manual

NITRATE MANIFOLD DIAGRAM



Sample Loop = 17 cm
QC8000 Sample Loop = 22.5 cm

Interference Filter = 520 nm

CARRIER is DI Water.

All manifold tubing is 0.8 mm (0.032 in) I.d. This is 5.2 uL/cm.

7 is 135 cm of tubing on a 7 cm coil support

APPARATUS: An injection valve, a 10 mm path length flow cell , and a colorimetric detector module is required.

Note 1: This is a 2 state switching valve used to place the cadmium column in-line with the manifold.

LAUCKS TESTING LABORATORIES INC.
Seattle, Washington

SOP #:LTL-9202

Title: **Total Suspended Solids (Non-Filterable Residue) Using EPA Method 160.2 / Standard Methods 2540D and Total Volatile Suspended Solids Using Standard Methods 2540 E.**

Revision history:

Number	Date
1.0	7/11/94
2.0	3/7/97

UNCONTROLLED

Written by: Harry Romberg Date: 3-7-97
Harry Romberg, Quality Assurance Officer

Reviewed by: Bill Lundberg Date: 3/7/97
Bill Lundberg, Inorganic Conventional Chemistry Manager

Approved by: Karen J. Kotz Date: 3/7/97
Karen Kotz, Laboratory Director

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1. Introduction and Scope

1.1 Method Description

1.1.1 Scope and Application

1.1.1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The practical range of the determination is 4 mg/l to 20,000 mg/l. The detection limit, however, is generally reported as 2 mg/l unless a sample volume greater than 100 mls is used.

1.1.1.2 A well-mixed sample is filtered through a standard glass fiber filter. The filter and residue are dried to constant weight at 103°C-105°C.

1.1.1.3 The filtrate from this method may be used for Total Dissolved Solids (Filterable Residue).

1.1.1.4 If volatile suspended solids are to be determined, the filter and residue are then ignited at 550°C and the loss on ignition determined.

1.1.2 Interferences

1.1.2.1 Samples high in dissolved solids (filterable residue), such as saline waters, brines and some wastes, may be subject to positive interferences due to soluble material which has not been adequately washed from the filter. Care must be taken to ensure that an appropriate filtering apparatus has been selected and the filter adequately washed in order to minimize this possibility.

1.1.2.2 Samples which are very high in suspended material or which have certain particle sizes may plug the filter causing difficulty in filtering. It may be necessary to reduce sample size in order to reduce this tendency.

1.1.2.3 This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

1.2 Sample Collection, Sample Storage, Holding Times

1.2.1.1 No preservation of the sample is necessary. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is required. Analysis should begin as soon as possible and should in no case exceed 7 days from the date of collection. All exceptions, whether due to laboratory or client cause, must be recorded on a Holding Time Violation Report (HTVR).

1.3 Definition of Terms

1.3.1 This section defines terms and acronyms as they are used in this SOP. Other terms, such as MS/MSD or method blank, are not defined here since it is assumed that the user of this SOP already understands their more general meaning.

DIW - Deionized water - Lab reagent water. This water should be free of virtually all analytes.

MDL - Method detection limit - The lowest concentration a sample which will yield a positive result that is greater zero at a known level of confidence. MDLs are empirically determined by Laucks, although there is no known way to determine the MDL for the TSS or TVSS analyses.

SRM or LCS - Standard Reference Material or Laboratory Control Sample. This is a material of approximately the same matrix as the samples, containing a known and usually certified amount of target analyte and which is prepared and analyzed in the same manner as a typical sample. This sample is used to demonstrate that the analytical system is in control. It may be considered to be a blank spike for most inorganic analyses and is preferred over artificially spiking blank materials. This type of sample is rarely analyzed at Laucks for TSS and there is no known source of TVSS material.

Sequence - A set of samples analyzed in a chronologically continuous group.

Total Suspended Solids (TSS) (nonfilterable residue)- Those solids which are retained on a glass fiber filter of the appropriate retentive ability and dried to constant weight at 103-105C.

Total Volatile Suspended Solids (TVSS) - Suspended solids which are volatile (burn off) at a temperature of 550°C.

2. Equipment List

Glass fiber filter discs, 4.7 cm without organic binder, Gelman A/E or equivalent. Laucks currently uses Pro Weigh 47 mm glass fiber filters from Environmental Express which are designed for TSS analysis. They are pre-washed and pre-weighed and require no additional preparation.

Membrane filter funnel with the capability of adequately supporting 4.7 cm. filters

Suction flask

Drying oven, set at 103°C-105°C.

Muffle furnace set at 550°C ± 50°C

Desiccator charged with active silica gel desiccant

Analytical balance, capable of weighing to 0.1 mg.

3. Safety precautions and Waste Disposal

3.1 Safety Precautions

3.1.1 All standards, samples and sample solutions should be handled as if they are hazardous substances.

3.1.2 Refer to the instrument manufacturer's manual for routine instrument precautions.

3.1.3 Routine precautions include an awareness of the moving parts on the instrument you're using. These parts are often charged with power from an electrical component or with high pressure gas and have the potential to do harm if not used properly.

3.1.4 Electrical shock - All instruments present the possibility of electrical shock The operator should take all precautions including ensuring that all instruments are operated with fully grounded power outlets, turning off the instrument and disconnecting the instrument from the electrical power supply before working on any electrical components, etc.

3.1.5 Routine precautions include an awareness of elevated temperatures of both the oven and any samples which have recently been removed from the drying oven or especially the muffle furnace. The temperatures involved in this analysis can cause severe burns if adequate care is not taken.

3.2 Waste Disposal

3.2.1 No waste should be generated from this procedure. Sample residues may be washed out and discarded down the sink.

4. Quality Control

4.1 Method Blanks

4.1.1 Criteria:

4.1.1.1 Method blanks are used to verify contamination free reagents and apparatus. They are prepared with every set of samples prepared at the same time or at least one blank every 20 samples which ever is more frequent. The method blank is prepared by pouring the same amount of deionized water through a filter as one would a typical sample (generally 100 mls.). Any TSS above the detection limit is reported. Method blank control limits are such that contamination should not exceed twice the detection limit. If 100 ml samples are used, Laucks generally considers the detection limit to be 2 mg/L with method blank control limits of 4 mg/L.

4.1.1.2 In making a determination of whether or not the analysis is in control, the analyst should actually be normalizing the blank to whatever volume was used for any sample. It is assumed that any blank is due to washings from the filter and apparatus and is actually independent of sample volume. In other words, the control limit for this analysis is actually 0.4 mg. If blank contamination exceeds that value, the TSS (or TVSS) of samples must be ten times that weight or corrective action should be taken.

4.1.1.3 If TVSS is being determined, the filters are processed in the same manner only are also heated to 550°C. Otherwise, the detection limits, criteria, and corrective actions are the same as for TSS.

4.1.2 Corrective action

4.1.2.1 Corrective action may necessitate re-preparation and re-analysis of the sample set. For example if TSS or TVSS were found in the blank but not in any of the associated samples, then the sample group may not require re-analysis. In addition, if sample levels exceed 10 times the blank, the level of contamination may be considered insignificant. In any case, if re-analysis is not being undertaken, the analyst must first discuss the issue with the Quality Control Officer. In all cases where blank contamination exceeds the control limit, a narrative comment must be made which documents the corrective actions taken.

4.2 SRM or LCS

4.2.1 Criteria

4.2.1.1 Analysis of a reference material is not normally required for TSS analysis and no known material is available for TVSS. An SRM/LCS analysis will generally be analyzed only if specifically required for a project. If not otherwise specified in that contract, it would typically

be analyzed at a frequency of once per 20 samples. Vendor specified control limits would be used for any such material.

4.2.2 Corrective Action

4.2.2.1 Re-analysis of all associated samples may be required if this sample exceeds it's limits. The QC Officer should be consulted for any other corrective actions and all instances of out-of-control events and any actions taken must be documented in the QC narrative of the report.

4.3 Sample Duplicate

4.3.1 Criteria
At least one duplicate sample per 10 samples is required. RPD values are calculated as follows:

$$RPD = \frac{|S1 - S2| * 100}{(S1 + S2)/2}$$

where
S1 = measured concentration in the initial analysis
S2 = measured concentration in the duplicate analysis

4.3.1.1 The RPD control limits are detailed in the Quality Control Database (QC_DB) and will change from time to time. For samples with values which are less than 5 times the detection limit, the control limit is equal to 5 times the detection limit. For values greater than 5 times the detection limit, the control limit is a calculated percent RPD.

4.3.2 Corrective action

4.3.2.1 If a trend in out of control RPD values is observed, the methods used must be examined to determine the source of variance. Once this source is identified, the method must be changed so that samples can be analyzed with a predictable reproducibility. If integrity of reported sample values is in doubt, re-analysis of all associated samples may be called for. Corrective actions should be discussed with the Quality Control Officer.

5. Operation procedures

5.1 Sample Analysis

5.1.1 Analysis sequence

Method Blank
SRM or LCS (if required)
up to 20 samples plus duplicates

5.1.2 Analytical Operation

5.1.2.1 Preparation of glass fiber filter disc if Environmental Express Pro Weigh filters are being used: Remove the filter from it's aluminum weighing dish and place the disc on the membrane filter apparatus with the wrinkled side up. While vacuum is applied, rinse the disc with a small amount of deionized water in order to seat the disk in the filter device.

5.1.2.2 Preparation of glass fiber filter disc if pre-washed and pre-weighed filters are NOT being used: Place the glass fiber filter on the membrane filter apparatus (if 4.7 mm filters are being used) or insert into bottom of a suitable Gooch crucible (if 2.4 cm filters are being used) with the wrinkled surface up. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus (if 4.7 mm filter) or both crucible and filter if Gooch crucible is used, and dry in an oven at 103°C-105°C for one hour or at 550°C ± 50°C if TVSS is to be determined. Remove to desiccator and store until needed. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg). Weigh immediately before use. After weighing, handle the filter or crucible/filter with forceps or tongs only. As in the procedure for the pre-weighed filters above, wet the filter slightly before use in order to properly seat it in the filtration apparatus.

5.1.2.3 Assemble the filtering apparatus and begin suction, taking care to have wet the filters as described in either procedure above. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml graduated cylinder. If this volume takes longer than 5-10 minutes to pass through the filter, sample volume must be reduced such that the filtration time will not be exceeded. If that volume is less than or equal to 10 mls, it should be dispensed with a 10 ml Mohr (graduated glass) pipet which has a wide enough tip opening so as not to inhibit the passing of solid pieces of material.

5.1.2.4 Filter the sample through the glass fiber filter, rinse the graduate and filter with three successive 10 ml portions of deionized water, allowing the rinsate to pass completely through the filter between washings, and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.

5.1.2.5 If the sample contains large pieces of material which make it difficult or impossible to achieve a representative, homogeneous sample, it may be necessary to thoroughly mix the sample in a blender prior to filtration. If this is done, however, care should be taken to assure that air bubbles aren't entrained in the measured sample volume to the extent that it could affect the actual volume dispensed. In other words, let the bubbles and subsequent foaming subside before dispensing the sample.

5.1.2.6 Carefully remove the filter from the filtration device, taking care not to leave pieces of filter on the support apparatus, and place it in the aluminum weighing dish appropriate to that filter and sample.

5.1.2.7 Dry the filter for at least one hour at 103°C-105°C.

5.1.2.8 Remove the filter and aluminum dish from the oven and place in a desiccator to cool. The samples MUST be cooled prior to weighing or the apparent weight will be affected.

5.1.2.9 Repeat the cycle of drying, desiccating, cooling and weighing until the filter/dish attain a constant weight, changing by no more than 0.5 mg.

5.1.2.10 Record the final weight for calculation of TSS.

5.1.2.11 If TVSS is to be determined, repeat steps through using a muffle furnace pre-heated to 550°C ± 50°C. Record the final weight for calculation of TVSS.

5.2 Quantification

5.2.1 Residue concentrations are calculated using the following equations:

$$TSS = \frac{(W_f - tare) \times 1000}{V_i}$$

$$TVSS = \frac{W_f - W_a \times 1000}{V_i}$$

where:

V_i = volume of sample used in mls
W_f = weight of dried residue & filter
W_a = weight of ignited residue (after ignition @ 550°C) & filter in mg
tare = tare weight (weight in mg of filter before filtration of sample)

5.2.2 TSS and TVSS are generally reported on a mg/L as received basis.

6. Reports

6.1 Data Packet Organization

6.1.1 The data package for this analysis consists of the data sheet and a quality control database (QC_DB) report form.

6.2 Quality Control Reports

6.2.1 All results for quality control tests are entered into the lab data base using the QC_DB program. Printouts of all data entered need not be included in the package. However, all must be referenced on the report form. This includes the blank and duplicate results and any other QC which might have been analyzed by special request (such as an SRM/LCS).

6.3 Sample Result Reports

6.3.1 Data Qualifying Flags

6.3.1.1 Sample report results are qualified with data qualifying flags. These flags have the following definitions:

CODE	Definition
U	: The analyte of interest was not detected, to the limit of detection indicated.

Appendix I

QC Summary Table

Laucks Testing Laboratories

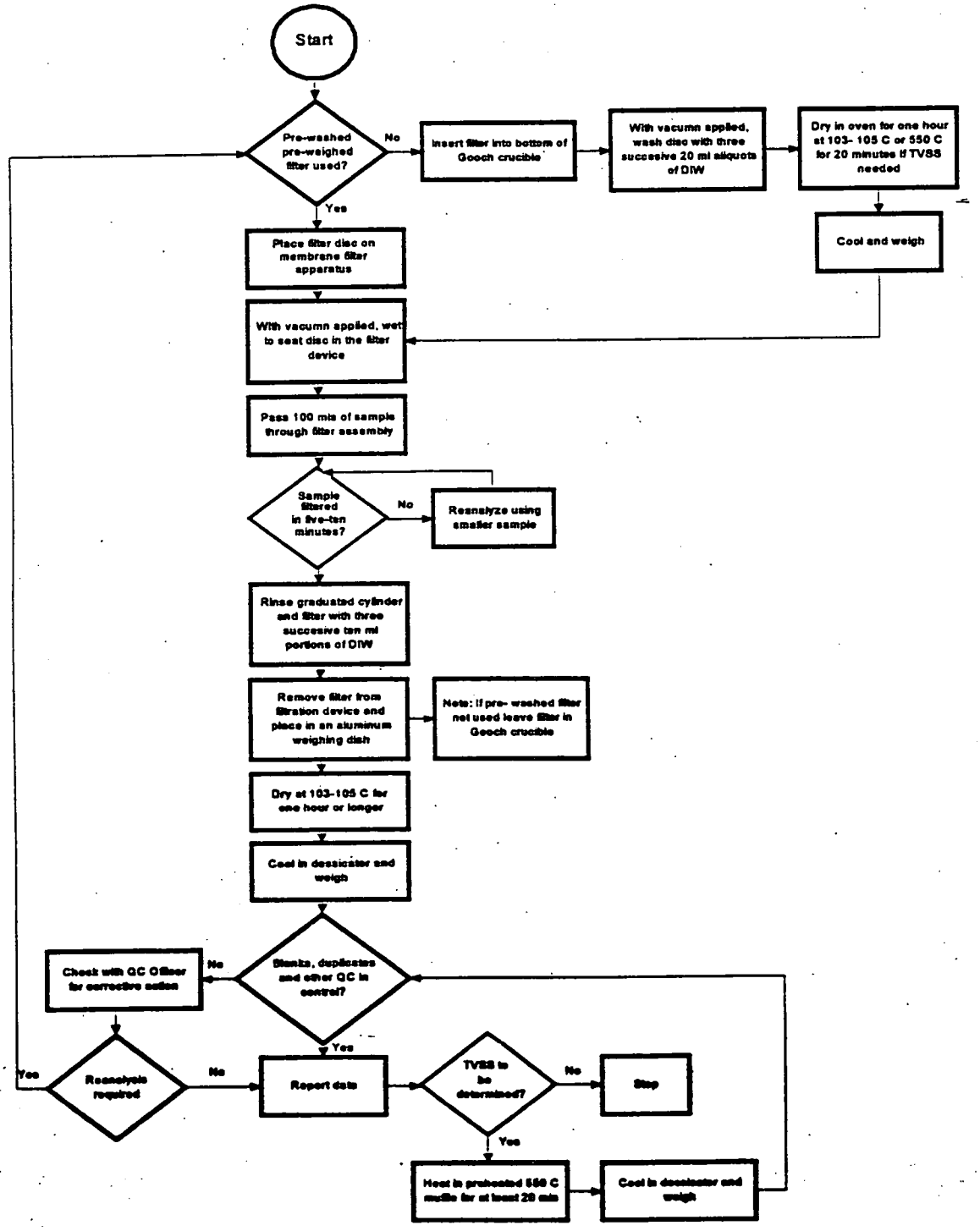
Method EPA 160.2 / SM 2540D & E QC Requirements and Corrective Actions

QA Element	Method Criterion	Laucks Criterion	Frequency	Corrective Action	Documentation
Method Blank	None	<4 mg/L or no more than twice the detection limit	5% frequency (1 per 20 samples)	Re-analyze all samples <10x the actual weight of the solids. Consult QC Officer for any other actions	QC_DB report form with appropriate commentary
Duplicate % Difference	None	See current control limits catalog or QC_DB database	10% frequency (1 per 10 samples)	Discuss with QC Officer. If impact appears serious, may need to re-analyze samples	QC_DB report form with appropriate commentary
Standard Reference Material (SRM) Recovery	None	Within vendor supplied limits or 90%-110% recovery	If required, at frequency specified, or 5% if not specified	Discuss with QC Officer. If impact appears serious, may need to re-analyze samples	QC_DB report form with appropriate commentary

Appendix II

Flow Chart

Total Suspended Solids (TSS) and Total Volatile Suspended Solids (TVSS)
EPA 160.2 and/or SM 2540D&E



Standard Method 2340 B: Hardness by Calculation

1.0 Discussion

The preferred method for determining hardness is to compute it from the results of separate determinations of calcium and magnesium.

2.0 Calculation

Hardness, mg equivalent $CaCO_3$/L = 2.497[Ca, mg/L] + 4118[Mg, mg/L]

TRIANGLE LABS

January 29, 1999

Triangle Laboratories, Inc.
SOP Release Information

The following SOPs have been requested by Laucks Testing and are being released for use in the CTO 10 QAPP for upcoming work at the Crane site. The SOPs are considered confidential and proprietary by Triangle Laboratories. Further use of the SOPs will need to be authorized by Mr. Don Harvan at Triangle Laboratories. He can be contacted at 919-544-5729. Any unauthorized reproduction or distribution is strictly prohibited and shall be considered a misappropriation.

Released to: Terrie Baranek
ECT. CON , Inc.
35313 Fox Chase Drive
Imperial, PA 15126
(724)698-8042

If there are further questions about the SOPs, please do not hesitate to contact me at 919-544-5729 x269.

Sincerely,

Mary C. McDonald
Project Scientist

Triangle Laboratories, Inc.
801 Capitola Drive
Durham, NC 27713-4411
919-544-5729
P.O. Box 13485
Research Triangle Park, NC 27709-3485
Fax # 919-544-5491

Triangle Laboratories, Inc.
SOP Release Form

Released to:

Name: Terrie Baranek (fr. Lauks Testing)

Company: ECT. CON, Inc.

Location: Imperial, PA

Released by:

Name: Mary C. McDonald

Date: 1-29-99

Mgmt Approval: Dan Horvan 2/1/99

The attached standard operating procedures (SOPs) contain information ("Information") with independent actual or potential commercial value which is not readily known or ascertainable by Triangle Laboratories' competitors and others. This information and these SOPs are confidential to Triangle Laboratories, Inc. and may not be disclosed to any person other than the designated recipient(s) without prior written authorization from Triangle Laboratories, Inc. Any unauthorized reproduction or distribution is strictly forbidden and shall be considered a misappropriation.

Attached SOPs:

SOP ID	Version	SOP ID	Version
DSP 161			
DHR 182			
DSP 105			

Original: QA Department Copy: Client

U:\forms\ 0101-22.frm (1/20/99)

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QUALITY ASSURANCE INSPECTIONS

TLI SOP No. 2.02	Version: 1	Effective Date:	June 11, 1996
Author:	Patty Ragsdale	Date Written:	May 28, 1996
Technical Approval:	QA Manager	Date Approved:	6/10/96
Authorization:	General Manager	Date Authorized:	6/10/96

I. **Scope and Application**: The purpose of this SOP is to describe the system of inspections employed by the Quality Assurance Department to ensure proper adherence to established policies, procedures and regulations by the operating staff. All laboratory records, personnel, procedures and equipment are subject to inspection as outlined in this SOP.

II. **Responsibility:** Audits are performed by members of the Quality Assurance Department. The applicable project scientist is responsible for ensuring implementation of necessary corrections for work regulated by the U.S. Environmental Protection Agency Good Laboratory Practices (EPA GLPs) or by the U.S. Food and Drug Administration Good Laboratory Practice (FDA GLP) regulations. Department supervisors are responsible for ensuring implementation of necessary corrections for non-GLP regulated work. Management shall review all inspection reports.

III. **Procedure:**

A. Frequency

1. Each laboratory section will be audited through the internal inspection process at least once a quarter.

2. Work regulated by the EPA GLP or by the FDA GLP regulations must be inspected a minimum of once during the course of a study. To ensure that each study is conducted in accordance with the applicable regulations and with the applicable protocol the following procedure is followed:

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a) The Quality Assurance Department serves as the Quality Assurance Unit (QAU) defined in the GLP regulations.

b) The QA department is notified of all pending studies.

c) The QA staff identifies the critical phases of each study and identifies which elements will require inspection. The operating staff is then responsible for communicating work schedules to the QA staff so the inspection schedules can be met.

d) Long term studies are inspected throughout the life of the study. Steps b) and c) are repeated with each shipment of samples until the study has been completed.

B. Audit Types:

An audit may consist of one or more of the following: (1) traceability audit, (2) phase inspection, (3) data audit, and (4) documentation inspection. Additional types of audits may be added any time the Quality Assurance staff or management determines a need to do so.

1. Traceability audit

a) This type of audit tracks samples and related documentation from receipt to archival storage or disposal.

b) A sample is selected from the chain-of custody (C-O-C) and traced, matching all entries on the C-O-C to the laboratory records. Reagents and standards referenced in the documentation may also be traced to original materials using just the laboratory records.

c) Any breaks in the documentation, i.e. uses that cannot be verified through primary documentation, are included in the inspection report.

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2. Phase Inspection

   a) Inspection of a procedure as it is performed on samples with real-time comparison of technique and application to the applicable SOP(s) and/or protocol/method.

   b) Actual practice versus written procedure and documentation are of particular interest. The inspector verifies each action observed with the applicable protocol. Undocumented deviations are included in the inspection report.

   c) During this type of inspection, equipment calibrations are verified as applicable, as are reagent and standard preparations and documentation.

3. Data audits - GLP regulated studies

   a) All interim data reports are subject to inspection. These inspections consist of, but are no limited to, the following:

      (1) Standard curve calculations are independently verified.

      (2) A minimum 10% of all sample, calibration standard, and QC sample data are selected for calculation verification and are compared to raw data. Note: Percentage may increase based on client requirements.

      (3) All QC and calibration standards are reviewed for acceptance criteria.

      (4) Raw data is reviewed for FDA GLP compliance.

   b) All draft summaries and final data reports are inspected prior to release to the client. These inspections consist of, but are not limited to, the following:

      (1) All elements required by the regulations are present.

      (2) All sample, calibration standard and QC sample IDs are compared to primary records.

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(3) All sample, calibration standard and QC sample concentrations are compared to the verified interim reports.

(4) All regression constants are compared to the verified interim reports.

(5) All repeated analyses are reviewed and must be accounted for in the text of the report.

(6) A minimum 25% of all summary statistics are verified through independently calculation.

(7) Outlier test properly applied and outlier data properly noted.

(8) Facts contained in the report are verified via primary laboratory records.

(9) Laboratory records are reviewed and compared to the final report to verify the accuracy of the representation of work performed.

4. Data audits - non-GLP regulated studies

a) A random sampling of completed reports are selected and reviewed by the QA staff daily.

b) Errors found are reported to the applicable area supervisor.

c) Trends in problem communication and observed trends in the data will result in the initiation of corrective action reports as necessary.

d) A record of each reviewed report and associated observations is maintained by the QA Department.

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5. Documentation inspection

   a) Inspection of logbooks, worksheets, and reagent records to ensure proper documentation practices.

   b) Errors and/or gaps in the records are included in the inspection report.

C. Audit Documentation

1. A formal report of each inspection is prepared. In the case of data audits, the reviewed copy of the report showing which elements were checked is signed and dated by the reviewer and maintained as part of the inspection report.

2. Inspection reports are submitted to the area supervisor (non-GLP regulated work) or to the appropriate project scientist (GLP-regulated work). After all findings have been addressed and the actions taken have been accepted by the QA staff, each final report is reviewed by the Management designee. In the event of critical findings, the inspection report is reviewed by the Management designee prior first and again after resolution by the operating staff.

3. All completed inspection reports are maintained by the QA Department. Inspection activity may be viewed and verified by non-TLI auditors through review of the cover sheets which bear signatures and dates of the inspection, report issuance, and review by project scientist, operating staff and by management. Other sections of the inspection reports may not be viewed by non-TLI personnel.

Original stamped in blue:

ORIGINAL

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NON-CONFORMANCE			
TLI SOP No. 2.04	Version: 3	Effective Date:	11/30/98
Author:	Bel Rueda	Date Written:	October 20, 1998
Authorization: Phil Albro Management		Date Authorized:	11/20/98

I. **DEFINITION:** A Non-Conformance is the failure to comply with one or more criteria established for the acceptance of data.

II. **SCOPE AND APPLICATION:** The purpose of this SOP is to describe the decision and documentation process applied to non-conformances or analytical elements which fail to meet the applicable acceptance criteria. This SOP applies to all analytical data and associated data reports, and must be followed by all members of the TLI staff.

III. **RESPONSIBILITY:** The staff member who identifies a non-conformance issue proposes an action plan and records it on the Non-Conformance Report (NCR). The Area Manager evaluates the appropriateness of the proposed actions and potential impact on other data prior to approving or rejecting the proposed actions. The QA Department evaluates the issues and determines whether there is a need for additional quality control measures.

IV. **PROCEDURE:**

A. When analytical data do not satisfy the acceptance criteria (allowable or unallowable exceptions), an NCR must be completed by the staff member identifying the issue. The issue and proposed actions are discussed initially with the area team leader or senior technical analyst.

B. NCRs resulting from defined allowed exceptions are reviewed and accepted by a team leader or the area manager. Allowed exceptions are defined in the written guidelines for each work area.

C. Completed NCRs, which are not associated with defined allowed exceptions, must be forwarded to the Area Manager (or a representative of senior management) for review and acceptance. The Area Manager evaluates the proposed actions and the potential impact on other data and signs the report denoting approval.

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D. If the proposed actions are not appropriate, technical guidance is sought from the Area Manager or appropriate member of senior management until the issue is adequately resolved.

E. Verbal acceptance may be given after full discussion of the NCR issues. In such cases, the person on-site must document the verbal acceptance and the manager who granted the acceptance must verify the verbal acceptance by signing the NCR document as soon as possible.

F. Data associated with an NCR must not be reported to the client until the NCR has been accepted.

G. Each NCR shall include the following:

1. Name of the persons identifying and resolving the non-conformance;
2. Date the non-conformance was identified;
3. Identification of the affected project data;
4. A description of the failure or non-conformance;
5. A description of the planned actions, action associated with the investigation, and resolution of the non-conformance; and
6. Conclusions regarding the impact of the non-conformance on other project data.

H. Data on the NCRs shall be documented as required in the SOP for recording raw data.

I. Copies of sufficient supporting data shall be attached to the NCR. This data shall be sufficient to identify the issue, reconstruct the actions taken, and evaluate the appropriateness of these actions. This data must also include the identities of the persons responsible for sample preparation and analysis.

J. After securing the approval signature, the original NCR and any supporting data not already in the project file are placed in the project file. A copy of the NCR and copies of all the supporting data are forwarded to the Production Technical Assistant. The data copied must be sufficient to reconstruct the issue, actions taken, and impact on associated and other project data.

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Non-Conformance Report

____ Project ____ Calibration Standard Other _____

Item ID _____

Describe Non-Conformance:

EXAMPLE

Describe Impact of Non-Conformance:

Actions Taken:

NCR and associated actions accepted by _____
Signature Date

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SAMPLE RECEIPT, IDENTIFICATION, HANDLING AND STORAGE

TLI SOP No. 5.01	Version: 8	Effective Date:	12/14/99
Author:	Anzor Gatchetchiladze	Date Written:	December 1, 1999
Authorization: Valerie Evans Management		Date Authorized:	12/7/99

I. **PURPOSE:** To describe the standard operating procedures (SOPs) to be followed to ensure sample security and integrity from the time of receipt to the time of final disposition. This includes procedures for sample inspection, log in, storage, archival, disposal, shipment and the initiation and usage of a chain of custody (COC) form for all sample movement while at Triangle Laboratories, Inc. (TLI).

II. **SCOPE:** The procedures described in this SOP are applicable to all samples that are received by TLI. In addition to the received sample, for this SOP, sample also refers to any composites, subsamples, or extracts generated from said sample.

III. **RESPONSIBILITY:** The primary responsibility for sample security and integrity belongs to the Sample Custodian or designated alternate(s), who initiates the procedures described in this SOP. However it is the responsibility of all personnel at TLI, who handle samples, to ensure the security and integrity of the samples under their control and to document on a COC form the movement of those samples.

IV. **SAFETY CONSIDERATION:** Incoming samples may contain harmful substances. Gloves, lab coat, and safety glasses must always be worn when handling samples. Some situations may require wearing a respirator. These situations include the receipt of leaking or highly volatile samples, or certain samples for which specific hazards are known prior to receipt. For samples of specific known hazards, refer to the appropriate appendix in this SOP for additional handling instructions. See Appendix A for handling potentially radioactive samples, Appendix B for handling samples contaminated with the hantavirus, and Appendix C for handling human blood and other potentially infectious material (OPIM). For additional safety information, consult the Safety and Health Officer or the "Safety and Health Manual".

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V. PROCEDURES:

NOTE: Special instructions from study specific protocols or EPA methodology supersede this SOP.

A. SAMPLE RECEIPT:

1. At the time a sample shipment is received, the receiving individual will document, the time and date received, who received it, and the general condition of the package(s).

   When the customer delivers the samples, also document the name of the individual making the delivery.

2. Open shipping container and carefully take all the samples out of the container. Take temperature of the samples (see paragraph B.3 of this SOP). Immediately count all the samples in the shipment and document on the Shipping Container Internal Custody Form (applies only to pharmaceutical samples). Examine all the documentation arrived with the shipment such as the Chain-of-Custody Report, Specimen Shipment Verification Form, Sample Traffic Report Form, etc. Verify and confirm that number of actual samples in the shipment matches the number of samples indicated in the paperwork.

   NOTE: If any discrepancy is found between the actual sample count and the shipment paperwork, stop the log-in process and notify the appropriate Project Scientist and the Sample Management Coordinator immediately. Follow instructions from the Project Scientist on how to proceed with the sample log-in.

   a) If the external documentation indicates that the samples could potentially be radioactive, refer to Appendix A for specific instructions.

   b) If the external documentation indicates that the samples could potentially be contaminated with the hantavirus (i.e. deer mice, squirrels, cotton mice, field mice, etc.), refer to Appendix B for specific instructions.

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Notify the appropriate Project Scientist or Customer Service Representative immediately. It is the responsibility of the Project Scientist or Customer Service Representative to contact the client so tracing procedures can be implemented.

NOTE: At this point, if samples cannot be processed immediately, place the shipping container(s) in the appropriate cold storage location (See section D). It is not necessary to place frozen samples in the freezer if there is sufficient dry ice in the shipping container to keep the samples frozen until full inspection and log in can be performed. Document when and where the shipment was stored.

3. Take the shipment to the designated sample receiving area to be inspected and logged in. If the receiving individual does not perform the inspection/log in or the sample shipment was stored prior to inspection, document when and by whom the inspection/log in was performed.

   NOTE: All the samples must be logged-in within 24 hours of receipt unless instructed otherwise by Sample Management Coordinator or a Project Scientist.

4. Create a project number for each group of samples received via the TLI electronic laboratory information management system. Project numbers are assigned sequentially by the system.. For samples of specific known hazards, follow the handling instructions detailed in the appropriate appendix for sample inspection and log in.

   NOTE: Only the Sample Custodian or a designated alternate may open sample shipping containers.

B. SHIPMENT INSPECTION: The inspection of each shipment is documented via the TLI electronic laboratory information management system, referencing the appropriate project number on each shipping document. Items to be documented include, but are not limited to the following:

1. Shipping Container(s)

   a) Presence/absence of custody seals

   b) Condition of custody seal - intact/broken

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c) Description of shipping container (e.g. ice chest, Styrofoam cooler, box) and its general condition

d) Carrier and airbill number(s)

e) If variations occur between shipping containers for the same project, itemize the samples in the receiving records according to the shipping container in which they arrived. Document items listed in section V.B.1.a - c as well as the status of preservation/temperature conditions (section V.B.3.) for each itemized sample group.

2. Shipping Documents

a) Presence/absence of client COC.

b) Presence/absence of Sample Management Office (SMO) forms for EPA samples.

c) Presence/absence of airbills and/or bills of lading.

d) Reference the TLI project number on the shipping documents.

3. Status of Preservation/Temperature Conditions

a) Presence/absence of coolant.

Is there frozen coolant present? Is there evidence that coolant was present but thawed en route? Is there no evidence of coolant ever having been present (i.e. shipped at ambient temperature)? Document what is observed.

b) Measure the temperature then document the condition as on ice, ambient, etc. For all samples received with some evidence of coolant (other than dry ice) and for samples to be analyzed by methods specifying preservation at 4 $\pm$ 2°C measure and record the temperature. For samples received on dry ice record on the Chain of Custody: "Dry Ice". No temperature should be recorded for these samples.

(1) If in doubt about preservation requirements/evidence of coolant, measure and record the temperature.

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(2) Measure the temperature of the temperature blank using a calibrated Infrared (IR) thermometer gun.

(3) If a temperature blank is no present, measure the temperature of a single randomly selected sample using the calibrated IR thermometer gun.

(4) NOTE: See Table 1 for common Emissivity values for materials.

(5) If the IR thermometer gun is unavailable for any reason, measure the temperature of the temperature blank (if present) with a calibrated Celsius thermometer. If no temperature blank is present, place an in-house temperature blank (a scintillation vial of deionized water which has been stored at approximately 4°C) in the shipping container (close the container) for at least one half hour and measure the temperature with a calibrated Celsius thermometer.

4. If the samples are not received under the specified temperature conditions, proceed with inspection and log in and notify the Project Scientist/Principal Investigator immediately to obtain further handling instructions from the client.

5. Sample Containers

a) Presence/absence of sample custody seals.

b) If wild rodent carcasses are present but not indicated on external documentation, immediately close and secure the sample container and notify the Health and Safety Officer (HSO).

c) Condition of the samples (intact, broken, leaking, etc.) and action taken, if applicable.

(1) Photograph unfavorable sample shipments and retain photos with the project records.

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(2) Salvage leaking or broken sample(s), when doing so will not increase the likelihood of further sample loss or contamination as follows:

(a) If a leaky sample is discovered, it may suffice to simply tighten the lid. Otherwise, treat it like a broken sample (Note loose lid on the COC).

(b) If a bottle containing a solid sample is cracked, but remains intact, wrap the bottle in aluminum foil and place the container in a plastic bag with a "zipper" closure.

(c) Isolate each broken sample into an appropriate new container, which is labeled with the client sample ID.

(i) Wrap fish and paper in heptane-rinsed foil, with the dull side towards the sample.

(ii) If a tube containing a biohazard sample is cracked, but the sample is still frozen and intact, place the tube in a clean beaker. Allow the sample to thaw, then transfer to a new labeled test tube.

(iii) For other matrices use a pre-cleaned 1 Liter amber glass bottle with a Teflon-lined lid or a clean container similar to the one which was damaged.

(3) Presence/absence of Contract Laboratory Program (CLP) tags and numbers. Tags are normally attached around the neck of the bottle they apply to. Document any discrepancies between the number on the tag and the client paperwork. CLP sample tags will be removed from the samples, placed in a sealed plastic bag, and transferred to the archivist for storage and/or shipment with the data package.

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(4) Notify the appropriate Project Scientist or Client Services Representative immediately of any damaged/unidentifiable samples. It is the responsibility of the Project Scientist or Client Services Representative to contact the client to obtain further instructions on how to proceed with the affected sample(s) and verify any known or suspected hazards associated with the affected sample.

(5) The Sample Custodian will properly dispose of samples that cannot be recovered, after the Project Scientist or Client Services Representative provides authorization.

6. Compare client COC, if present, with sample identification. Document any discrepancies between the sample identifications received and those on the client COC.

   Discrepancies include but are not limited to:

   a) Missing samples or samples present but not listed on the client COC.

   b) Missing information or differences in information contained on the sample tag and the client COC.

7. Notify the appropriate Project Scientist or Client Services Representative immediately of any discrepancies between the sample tag identifications received and those on the client chain of custody. It is the responsibility of the Project Scientist or Client Services Representative to determine if the discrepancies require client attention.

8. Return non-disposable shipment containers and coolant packs, which belong to the client, to the return address found on the airbill or client COC.

C. SAMPLE LOG IN AND IDENTIFICATION: Referencing the appropriate project number, the samples are logged into a "virtual logbook" within the TLI electronic laboratory information management system.

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1. The electronic laboratory information management system is used to assign a unique ID to each sample.

   a) The ID format is "Virtual Logbook" Number-Page Number-Sample Sequence Number.

   b) If a single sample is submitted in more than one container, each component is uniquely identified by appending sequential letters to the Sample Sequence Number.

2. For each sample, record the client sample identifier as stated on the sample, sample matrix, and the initial location, where the sample is to be stored.

   Record additional information such as assay codes, radiation measurements, imported soil, biohazard sample, etc., when applicable.

   Contact the appropriate Project Scientist or Client Services Representative for clarification, if the above information is unclear or unknown.

3. Securely label each sample with the TLI project number, the client ID, and the unique TLI ID. (It is a good idea to label both the container and the lid if there is space to do so without obscuring other labeling).

   In addition, imported soil samples and biohazard samples must be specifically labeled as such.

4. Subsequent IDs created for subsamples/aliquots taken for analysis are cross-referenced to the Log In ID and the client ID. All extraction glassware, auto sample vials, etc. containing sample must be properly labeled with a TLI ID.

5. Generate the Log In, TLI COC (Sample and Extract), and Project Communication forms as required for the project. Sign and date the COC.

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Contact the appropriate Project Scientist or Client Services Representative for clarification as to which formats are required if necessary.

6. The nature of the project determines the exact storage location of all original shipping and log in documents for the project.

   a) In all cases, documentation will be identified by project number and will be maintained in such a manner as to prevent destruction or loss (i.e. file cabinet, study binder, project file, etc.).

   b) Any copies of these documents will be clearly labeled as such and will be initialed and dated.

7. Notify the appropriate wet lab chemist of shipments containing samples, which require verification of other preservation measures (i.e. pH).

D. SAMPLE STORAGE:

1. Place samples in boxes or bags, as appropriate for the samples, labeled with the project number in such a way as to avoid breakage and cross contamination.

   a) Never store samples together with chemical standards in the same refrigerator/freezer.

   b) Always store samples for volatile analysis away from other sample types.

   c) Package untreated control samples separately from treated samples.

   d) For Pharmaceutical projects, note the location of the samples on the appropriate inventory list.

   e) Store Pharmaceutical samples in project designated freezers.

2. Actual storage requirements are dependent upon the matrix, the analysis requested, and client protocols or specifications. Store boxed samples in secure monitored storage locations which meet these requirements.

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a) Store sample extracts (except those designated for dioxin analysis, which must be stored at room temperature) in cold storage and protected from the light.

b) If necessary to prevent oxidation, flush the sample extract with dry nitrogen prior to sealing the storage vial.

E. SAMPLE TRACKING:

1. All personnel handling any sample (extract) at any time, from the time of initial receipt to the time of return or disposal, will document the movement of the sample on an internal COC form. Documentation includes:

   a) The identification of the sample being moved.

   b) The initials of the person who removed the sample from the storage location.

   c) When the sample was removed from storage.

   d) If applicable, when the sample was returned and if returned to a different location, the new storage location.

   e) Any additional information specified on the specific COC form.

2. In addition, the sample's whereabouts within the analytical process will be tracked via the electronic laboratory information system.

   NOTE: Copies of a COC must be clearly labeled as such and be signed and dated. Never update a copy of a COC. Entries must be made on the original document.

F. SAMPLE ARCHIVAL/DISPOSAL/RETURN:

1. Unless otherwise directed by the client, samples will be archived as follows:

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NOTE: It is the responsibility of the Project Scientist/Principal Investigator to provide the Sample Custodian with special instructions.

a) The received samples will be placed into archive storage (at ambient temperature) only after the analysis is complete, the data has been sent to the client, and samples in cold storage have remained there for at least 30 days or the project is canceled.

For studies involving multiple projects for a single report, samples are maintained in active storage until the client authorizes disposal or return.

b) Be sure lids are tight and place samples in box labeled with the project number. Fill each box before starting a new box.

c) Imported soil samples are archived separately from domestic soil samples and apart from other samples. This requirement is not needed if all solid samples waste disposal is performed by a contractor licensed to handle imported soils.

d) Write the date the box is full on tape affixed to the outside of the box. Use this date to determine when to remove the samples for disposal.

e) Document sample (extract) movement into archives on the appropriate form and if applicable, in the work area notebook.

f) In addition the sample's whereabouts within the analytical process will be tracked via the electronic laboratory information management system.

2. Sample disposal will be in compliance with state and federal regulations.

a) Dispose of samples at the direction of the client or following the applicable archive hold time.

b) Document sample (extract) movement on the appropriate COC form.

c) In addition, the sample's whereabouts within the analytical process will be tracked via the electronic laboratory information management system.

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3. Sample Return

   a) Obtain client authorization and packing/shipping instructions before returning any samples.

   b) Complete a COC and/or packing list for all samples being returned. One copy will accompany the shipment and a second retained for the project (study) file.

   c) Pack samples to prevent breakage and contamination according to client instructions.

   d) Document sample (extract) movement on the appropriate COC.

   e) In addition, the sample's whereabouts within the analytical process will be tracked via the electronic laboratory information management system.

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APPENDIX A

PROCEDURES FOR HANDLING POTENTIALLY RADIOACTIVE SAMPLES

I. **SCOPE AND APPLICATION:** The purpose of this document is to describe the procedures for the handling of potentially radioactive samples. Potentially radioactive samples are those samples that come from known radioactive material sites or client knowledge that the samples could be radioactive. Only those persons who have been trained in radiation protection by Duke University Radiation Safety Office (RSO) or the Safety/Health Officer of TLI are allowed to handle these samples.

II. **SAFETY CONSIDERATIONS:** Always wear protective gloves, coat and safety glasses when handling potentially radioactive samples.

All radioactive samples must have a label stating that they have been properly surveyed/wipes taken.

III. **PROCEDURES:** Incoming packages must be monitored as soon as possible after receipt, **but no later than 3 hours after receipt during normal working hours, or no later than 3 hours from the beginning of the next work day if received after working hours.**

The following procedures shall be performed if the incoming package is labeled as containing radioactive material, or if a package of radioactive material (not labeled) shows evidence of potential contamination, such as crushed, wet, damaged, etc.

A. Wipe tests will be performed on the radioactive samples/packages (inner and outer containers) for removable contamination using a Bicron Surveyor 50, with a pancake probe and/or SWGM, to measure the amount of radioactivity (if any) present. Wipes should cover an area of 300 sq. cm (7" x 7") and be taken on each surface of the package. If any wipes shows removable activity in excess of 220 dpm/sq. cm, see NOTIFICATION paragraph section III.I. All packages samples having an external reading greater than 2000 CPM or 2 mR/hr will be returned to the client. All radioactive samples/packages with survey readings of 2000 CPM or less will be further screened for radioactivity. Those readings should also be entered onto the log in record/chain of custody for each sample. If no radioactivity is present (background), then a range of .05 or less (mR/hr) should be entered on the log in record/chain of custody for each sample.

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B. Monitor each surface of the package. Note the location of the highest reading and take a reading at 3' from that point. If a surface reading in excess of 200 mR/hr or a 3' reading in excess of 10 mR/hr is detected, see NOTIFICATION paragraph below. If the package reads "Full Scale" from the surveyor when the selector switch is at 100x position, contact the Radiation/Safety Officer (RSO).

C. Next, remove packing slip and open outer package. Open inner package and verify that no shipping damage has occurred and that the contents agree in name and quantity with the packing slip. Wipe test inner package and contents. If packing slip does not agree with contents or contamination is found on the inner containers, notify the client and RSO. If the wipes taken from the sample container are greater than 2000 CPM or 2 mR/hr, contact the RSO and return those samples to the client.

D. If the wipes taken from the sample container are less than 2000 CPM, take the sample to the Sample Preparation Labs, take an aliquot of the sample (if applicable) and send to Duke University Radiation Safety Office for analysis using a Liquid Scintillation Counter.

E. If results from Duke University indicate that the sample is non-radioactive then analyze, extract and dispose of waste via TLI normal operating procedures.

F. If survey or results from Duke University indicate that the sample is radioactive, then analyze, extract and keep <u>all</u> waste associated with the sample together. The waste will be properly disposed of according to all applicable regulations or returned to the client.

G. Survey the packing material from the package in a low background area with an appropriate instrument. If no activity is detected, remove or completely obliterate all radioactive signs and labels and discard the box as normal trash.

H. The Sample Prep Lab(s) used to prepare <u>radioactive samples</u> will be surveyed daily using a Bicron 50 Surveyor with a pancake probe. Wipes will be taken monthly from that lab and sent to Duke University for analysis by using a Liquid Scintillation Counter.

I. NOTIFICATION: IF REMOVABLE SURFACE CONTAMINATION EXCEEDS 200 DPM/SQ. CM; RADIATION LEVELS EXCEED 200 mR/hr ON THE SURFACE OR 10 mR/hr AT 3': NOTIFY THE DELIVERY CARRIER, THE NC DIVISION OF RADIATION PROTECTION (919-571-4141) AND THE RSO.

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APPENDIX B

PROCEDURE FOR HANDLING RODENT SAMPLES POTENTIALLY CONTAMINATED WITH HANTAVIRUS

NOTE: CONTACT THE SAFETY/HEALTH OFFICER IMMEDIATELY. DO NOT OPEN THE SHIPPING CONTAINER UNTIL AUTHORIZED BY HIM/HER.

I. **SCOPE AND APPLICATION:** The purpose of this document is to outline the supplies and specific procedures for the safe handling of rodent samples (i.e. deer mice, squirrels, cotton mice, field mice, etc.) that are potentially contaminated with hantaviruses of significance to human beings.

II. **SUPPLIES REQUIRED:**

- Two half-mask respirators with organic vapor/acid gas/HEPA cartridges.
- Two non-vented splash goggles.
- Two tyvek coveralls.
- Two plastic splash aprons.
- Four pairs latex gloves.
- Commercially available chlorinated bleach diluted 1:10 with water. (10% bleach disinfectant) in a spray bottle.

III. **PROCEDURE:**

A. The samples will be delivered directly to Triangle Laboratories. Shipping containers will remain closed until they are ready for processing. Freezing of the entire unopened shipping containers is allowed if they arrive late in the day for processing during the subsequent six hours.

B. All processing of rodent samples will be done in a designated closed lab. Only individuals wearing the required protective clothing, and who have been certified for respirator use by the Triangle Laboratories Occupational Health-Respiratory Safety Program, are allowed in the room during specimen processing. These

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room access restrictions are removed after all rodent specimen processing has been completed, working surfaces have been decontaminated, contaminated disposables have been properly stowed, and the room has been aired out for at least 30 minutes.

C. Required protective clothing for specimen processing includes tyvek coveralls, a plastic apron, disposable boot covers, two pairs of latex gloves, non-vented safety goggles, and a properly fit half-mask respirator with organic vapor, acid gas/HEPA filter cartridges.

D. The animals **must** be packaged as follows:

1. Each individual animal must be packaged separately, even if compositing is required. The chain of custody should contain all compositing information. The individual animals will be ground first in methylene chloride. Compositing will take place once each animal has been ground and can be safely handled.

2. Each individual animal should be wrapped in two layers of aluminum foil, shiny side away from the animal. The outside of the foil encased animal should be labeled with the sample identification number.

3. Each foil encased animal should be placed inside a sealed ziplock bag that is also labeled with the sample identification (ID). This ziplock bag should then be placed inside another ziplock bag such that the seal from the inner bag is at the bottom of the outer ziplock bag. The outer bag should also be labeled with the sample ID.

4. If there are non-rodent samples collected at the same site, these must be shipped ***separately*** from the mice samples. This will allow the laboratory to effectively quarantine the infected samples prior to preparation.

E. For greatest efficiency, two technicians should participate in specimen processing. One technician will be considered "dirty" and will directly handle specimen bags and contents, while the other technician will be considered "clean" and will handle specimen log in forms, blender vessels and tops, and solvent. All direct contact (especially hands) and indirect contact (surfaces of

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items touched by "dirty" technician) between technicians should be avoided. These roles are not to be switched mid-processing.

F. After both technicians have donned their protective clothing and the doors to the processing room have been closed, the "dirty" technician should open the shipping container, being careful not to tear his/her latex gloves or tyvek suit.

G. The vertical safety sash on the chemical fume hood should be left in the lowered position to increase the inward linear flow-rate of the fume hood, thereby helping to contain and exhaust any aerosolized virus hazard.

H. The "dirty" technician should sit or stand to the right of the "clean" technician throughout the processing. He/she should remove a specimen from the shipping container, read and/or show the samples identification information to the "clean" technician for log in. The "dirty" technician should not touch the pen or any of the log in supplies.

I. The "clean" technician should load the appropriate amount of methylene chloride solvent into a clean blender vessel and hold it inside the hood work zone within reach of the "dirty" technician. The "dirty" technician should then open and hold the plastic bags containing the specimen and, without directly touching the rodent or the outside of the blender vessel, drop the rodent into the vessel containing the solvent.

J. The "clean" technician should then place a clean lid on the blender vessel, place the vessel on the blender motor, and emulsify the specimen for the appropriate amount of time.

K. The "dirty" technician should then place the empty specimen bags and associated potentially contaminated tags or packing material into the incineration waste container.

L. Steps G-J of this document, above, are then repeated until all specimens have been processed. After emulsification, the "clean" technician is allowed to decant the contents of each blender vessel into another container for storage, and may then remove the vessel from the fume hood work zone if necessary for cleaning and reloading of solvent.

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M. If a pair of gloves becomes torn at any time during this procedure, the gloves and any exposed human skin are thoroughly wetted with 10% bleach disinfectant in a continuous hand-washing like manner. If skin has been broken or penetrated by a potentially contaminated object, the gloves are removed after bleach disinfection, and the wound is washed under running water with disinfectant soap for no less than 5 minutes, after which appropriate medical attention is sought. If no injury to the skin has occurred, a new pair (two pair if necessary) of gloves are donned and the torn pair of gloves are placed in the incineration waste container.

N. All remaining packing material in the shipping container, including any transport ice packs, are then placed into the incineration waste container.

O. When all above steps have been completed, a spray bottle containing 10% bleach disinfectant is used to wet down the sash and horizontal surface of the fume hood, the outside of all other potentially contaminated work surfaces, the outer pair of gloves over the hands of both technicians, the inside and outside of the shipping container, and the spray bottle itself.

P. With gloves wet with bleach disinfectant, the "clean" and "dirty" technicians then grab the outer surface of their left glove with their right double-gloved enabling them to pull off the outer glove on their left hand and drop it into the incineration waste container. The dry inner glove of their left hand is now exposed, which they use to pull off the outer glove on their right hand by slipping a finger under the collared wrist area of the glove as they stand over the incineration waste container.

Q. Wearing the dry inner pair of latex gloves, the technicians should then remove, in the following order, their plastic apron, their disposable boot covers, their tyvek coveralls, their goggles, and their inner gloves (in the manner described above), placing each disposable clothing item into the incineration waste container as it is removed. Any splash contaminated area on their protective clothing should be sprayed with a 10% bleach disinfectant prior to removal. The incineration waste container is then closed and sealed.

R. The floor surface directly around the specimen processing area and shipping container is then sprayed with 10% bleach disinfectant.

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S. Wearing their respirators, the technicians then leave the specimen processing room and allow it to ventilate for at least 30 minutes before allowing room re-entry. Outside of the room, they remove their respirators and thoroughly wash their hands with soap and water.

T. The incineration waste container is processed for incineration at the next available opportunity.

U. **Subsequent processing of methylene chloride emulsified rodent specimens can then commence without any residual biohazard.**

IV. REFERENCES:

A. Weigler BJ. Zoonotic hantaviruses: new concerns for the United States. Journal of the American Veterinary Medical Association 1995; 206 : 979-986.

B. Mills JN, Yates TL, Childs JE Parmenter RR, Ksiazek TG, Rollin PE, Peters CJ. Guidelines for working with rodents potentially infected with hantavirus. Journal of Mammalogy 1995; 79 : 716-722.

C. Centers for Disease Control and Prevention. Hantavirus infection - southwestern United States: Interim recommendations for risk reduction. Morbidity and Mortality Weekly Report. 1993; 42 (RR-11) : 1-13.

D. Centers for Disease Control and Prevention. Laboratory management of agent associated with hantavirus pulmonary syndrome: interim biosafety guidelines. Morbidity and Mortality Weekly Report. 1994; 43 (RR-7) : 1-7.

E. Department of Health and Human Services. Biosafety in microbiology and biomedical laboratories. HHS (CDC) Pub. No. 93-8395, 3rd ed., 1993.

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APPENDIX C

PROCEDURES FOR HANDLING BLOOD AND OTHER POTENTIALLY INFECTIOUS MATERIALS (OPIM)

I. **SCOPE AND APPLICATION:** Procedures delineated in this document are to be applied whenever human blood or OPIM are handled.

II. **SAFETY CONSIDERATIONS:** In the handling of human blood samples or samples containing other human body fluids, it is essential that the precautions delineated below be followed without exception. Precautions must be followed consistently. The approach and procedures delineated below are those recommended by the US Center for Disease Control and Prevention (CDCP). The Hepatitis B (HBV) and the HIV and HTLV-III/LAV viruses (AIDs viruses) appear to be incapable of penetrating the skin. Infection may nevertheless occur as a result of blood or infectious fluids coming in contact with mucus membranes or open wounds. Any individual working with human blood or body fluids must undergo a HBV vaccination program, prove immunity or that a past vaccination is still satisfactory to prevent infection.

III. **PROCEDURE:**

Recommended precautions for handling all blood or other human body fluid samples must be appropriate to prevent contamination, regardless of the knowledge or the lack thereof regarding the infectious state of the media. In the laboratory environment, the greatest risk for transmission involves exposure to a needle or other sharp instrument contaminated with infected blood. Great care must therefore be undertaken to prevent possible transmission via a puncture wound (e.g. needle, sharp glass, etc.)

A. Standard Precautions

1. Handle all human blood and/or body fluids samples as potentially infectious regardless of possible knowledge to the contrary.

2. When working with raw human blood or other body fluids, all work must be done in a hood. Disposable gloves as well as protective eyewear and clothing must be worn. In addition, a disposable mask or face shield must be worn whenever procedures, that are likely to generate droplets or aerosols, are performed.

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3. Sharp items (needles, glass, etc.) having contacted blood or body fluids should be considered as potentially infective and be handled with extraordinary care. Minimize handling and thus risks associated with such items. Prevent accidental punctures.

4. Disposable syringes, glass pipets and plastic pipet tips should be placed in puncture resistant containers located as close as possible to the area in which they are being used. If work is being performed in a hood, place the disposal container in the hood, immediately next to or as close as possible to the hood.

5. Hands should be washed immediately and thoroughly with soap and water if contaminated with blood or following glove removal after work with blood or other human body fluid samples. Practice standard good hygiene procedures. Do not handle with contaminated gloves or hand anything a co-worker may handle unprotected (i.e. phone, doorknob, etc.).

6. Spills of blood or other body fluids should be immediately cleaned with soap and water or a household detergent. Individuals performing such cleaning must wear disposable gloves. A freshly prepared solution of sodium hypochlorite (tenfold dilution of off-the-shelf commercial bleach) solution should be used to wipe the area after cleaning in order to thoroughly disinfect the affected area. An alternative to this is to spray the area well with Lysol™.

7. In the event of an exposure (i.e. an accidental puncture wound with a sharp object having contacted blood), immediately wash the area thoroughly with a germicidal soap and water and contact your supervisor for the appropriate follow up procedures.

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TABLE 1: COMMON EMISSIVITY VALUES

Non-Metals

Material	Emissivity
Asbestos	.95
Asphalt	.95
Basalt	.70
Brick	.95
Carborundum	.90
Ceramic	.95
Clay	.95
Concrete	.95
Cloth	.95
Glass Plate	.85
Gravel	.95
Gypsum	.80-.95
Ice	.98
Ice Bath	.95
Limestone	.98
Organic Materials (food, plants, oil, some chemicals)	.90-.98
Paint (non-Al)	.90-.95
Paper (any color)	.95
Plastic (opaque, over 20 mils)	.95
Rubber	.95

Non-Metals

Material	Emissivity
Sand	.90
Snow	.90
Soil	.90-.98
Water	.93
Wood, natural	.90-.95

Metals

Material	Emissivity
Alloy A3003 Oxidized	.30
Brass:	
Burnished	.30
Oxidized	.50
Carbon:	
Unoxidized	.80-.90
Graphite	.70-.80
Iron:	
Oxidized	.50-.90
Rusted	.50-.90
Wrought, dull	.90
Lead:	
Roughened	.40
Steel:	
Oxidized	.70-.90
Cold rolled	.70-.90

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Project Code	Station No.	Month/Day/Year	Time	Designate: Comp.	Grab
0033F	DAF546	12/12/96	1245		

Station Location: GW-10

Samplers (Signatures):

Tag No. T1-

Lab Sample No.

ANALYSES	
BOD	
Anions	
Solids (TSS) (TDS) (SS)	
COD, TOC, Nutrients	
Phenolics	
Mercury	
Metals	
Cyanide	
Oil and Grease	
Organics GC/MS	
Priority Pollutants	
Volatile Organics	
Pesticides	
Mutagenicity	
Bacteriology	
PCB-680	X

Remarks:

Preservative: Yes ☐ No ☒

★ GPO: 812-721

EPA

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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ESTABLISHING METHOD DETECTION LIMITS

TLI SOP No.	CQA125 Version: 3	Effective Date:	June 5, 1997
Author:	Patty Ragsdale	Date Written:	June 3, 1997
Technical Approval:	Phil Albro Technical Director	Date Approved:	6/9/97
Authorization:	Stan Olson Production Manager	Date Authorized:	6/4/97

I. **SCOPE AND APPLICATION:** The purpose of this SOP is to describe the means of determining Method Detection Limits (MDL) for target analytes. The procedure may be applied to a variety of matrices. All sample processing steps (e.g., extraction, cleanup) of specific analytical methods must be included in the determination of MDLS.

II. **BACKGROUND:** MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix type containing the analyte.

III. **PROCEDURE:**

A. Estimate a detection limit using one of the following:

1. The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5. (Noise for GC Method 608 defined as matrix noise.)

2. The concentration equivalent of 3 times the standard deviation of replicate measurements of the analyte in reagent water. The analyte concentration should not exceed 5 times the estimated detection limit.

3. The lower region of the standard curve where there is a significant change in sensitivity, i.e. a break in the slope of the curve.

4. Known instrumental limitations.

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B. Prepare or purchase water that is as free of interferent and analyte as possible (blank water). Interferent free water is defined as a water sample in which the concentration of analyte or interferent is not detected at the method detection limit for the analyte of interest. An interferent is presupposed to be normally present in a representative sample of a given matrix, with the exception of analytes specified in particular methods i.e. methylene chloride for VOA.

C. If the MDL is to be determined in blank water prepare a standard in water at a concentration which is at least equal to or in the same concentration range as the estimated MDL. (The recommendation is between 1 and 5 times the detection limit.) Proceed to step 4.

1. If the MDL is to be determined in another matrix, ana-lyze the sample after preparation and determine if the measured level of analyte is in the recommended range. (1 to 5 times detection limit). If so proceed to step 4.

2. If the measured level is less than the estimated detection limit, add more analyte to bring it into the range of 1 to 5 times the limit and then proceed to step 4.

3. If the measured level is more than 5 times the detection limit, either prepare a sample with a lower level of analyte or the sample may be used if it does not exceed 10 times the MDL in water.

D. Take a minimum of 7 aliquots, (Analysis of 8 aliquots is recommended), of sample to calculate the MDL and process each through the entire analytical method. Make all calculation according to the defined method with the final results in the method reporting units.

NOTE: One of the 8 spiked aliquots can be excluded from the MDL calculations process only if a documented laboratory accident affected that one sample.

E. Calculate the variance (S^2) and the standard deviation (S) of the replicate measurements as follows:

$$S^2 = \frac{1}{n-1} \left[\Sigma X^2 - (\Sigma X)^2/n\right]$$

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$S = (S^2)^{1/2}$

F. Compute the MDL as follows:

MDL = t (S) where t is taken from table below

TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

number of replicates	degrees of freedom	t
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
∞	∞	2.326

G. Optional repetitive procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

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1. Take the MDL as established in step 6, spike the matrix at the calculated MDL and proceed through the procedure starting with step 4.

2. Use the S^2 from the current MDL calculation and the S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 in the numerator and the smaller S^2 value into the denominator.

$$\text{F-ratio} = \frac{S^2A}{S^2B} \quad \text{(this must be < 3.05)}$$

Then compute the pooled standard deviation by the following equation:

$$S\ \text{pooled} = \left[\frac{6S^2A + 6S^2B}{12}\right]^{1/2}$$

3. Use the S pooled as calculated in 7b to compute the final MDL.

MDL = 2.681 (S pooled)

H. Evaluate the calculated MDL values versus the method required detection limits. **NOTE:** The values cannot exceed the target detection limits (TDLs).

I. The MDL study must be specifically identified by Method number and each analyte in the appropriate method reporting units. The sample matrix must be noted and if a recovery standard was used its recovery must be reported. (We will use surrogate standards.)

J. MDL's are established annually by method and matrix.

K. The MDL study data is kept on file by the Quality Assurance Department.

NOTE: This SOP is based on Appendix B to Part 136 -Revision 1.11 from the Federal Register Volume 49, No. 209 dated Oct.26,1984.

Original stamped in blue: ORIGINAL

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PCDDs AND PCDFs BY HRGC/HRMS - METHOD 8290			
TLI SOP No. DHR182	Version: 6	Effective Date:	March 25, 1998
Author:	Wojciech Krol	Date Written:	February 9, 1998
Authorization:	Management	Date Authorized:	2/16/98

I. **SCOPE AND APPLICATION:** This method provides procedures for the analysis of polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologues; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologues; PCDFs) from extracts of samples prepared according to SW 846 Method 8290.

II. **SAFETY CONSIDERATIONS:** The 2,3,7,8-TCDD isomer has been found to be acenegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in the 2,3,7,8 positions are known to have toxicities comparable to that of 2,3,7,8-TCDD. Extreme care must be exercised in all handling of extracts and standards in the application of this SOP. For additional safety information, see the TLI Safety and Health Manual and the appropriate MSDSs.

III. **EQUIPMENT:** The High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (GC/MS/DS) equipment utilized for this analysis includes the following:

A. Gas Chromatographs: Hewlett Packard 5890 or 5890 Series II (equipped for temperature programming and capillary columns)

B. High Resolution Mass Spectrometers: VG 70 Series, VG 70-SE Series, VG Autospec.

C. Data Systems: VG Analytical PDP11 with 11-250 software or VAX Alpha with Opus 3.2 software.

D. <u>GC Injection Port</u> - The GC injection port is designed for capillary columns. Typically, 2 µL injection volumes are used unless otherwise noted.

E. <u>Gas Chromatograph/Mass Spectrometer(GC/MS) Interface</u> - The GC/MS interface components can withstand 350°C. The interface has been designed so that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. The GC column is fitted directly into the mass spectrometer ion source without being

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exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb the PCDDs and PCDFs. Vespel™, or equivalent, ferrules are recommended.

F. Mass Spectrometer - The static resolving power of the instrument must be maintained at a minimum of 10,000 (10 percent valley).

G. Data System - A dedicated data system is employed to control the rapid selected-ion monitoring (SIM) process and to acquire the data. Quantitation data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored including the lock-mass ion as a function of time) must be acquired during the analyses and stored. Quantitation may be reported based upon computer generated peak areas or upon measured peak heights. The data system is set to acquire data as low as 10 ions in a single scan. Table 1. presents a listing of the ions which are typically monitored. The data system is set to switch to different sets of ions (descriptors) at specified times during an HRGC/HRMS acquisition. The data system provides hard copies of individual ion chromatograms for selected gas chromatographic time intervals. It also acquires mass spectral peak profiles and provides hard copies of peak profiles to demonstrate the required resolving power. Measurements of noise on the base line are performed using the hard copies of individual ion chromatograms provided by the data system.

NOTE: The detector ADC zero setting must be set to allow peak-to-peak measurement of the noise on the base line of every monitored channel and allow for good estimation of the instrument resolving power.

H. GC Columns

1. In order to have an isomer specific determination for 2,3,7,8-TCDD and to allow the detection of OCDD/OCDF within a reasonable time interval in one HRGC/HRMS analysis, the 60 m DB-5 fused silica capillary column is used.

2. The 2,3,7,8-TCDF isomer must be confirmed on a 30 m DB-225 fused silica capillary column, when 2,3,7,8-TCDF is detected on the DB-5 column at a level greater than or equal to the target detection limit.

IV. STANDARDS:

A. Calibration Solutions Six nonane solutions containing 17 unlabeled PCDDs and PCDFs and 18 $^{13}C_{12}$ -labeled PCDDs and PCDFs at known concentrations are used to calibrate the instrument. The analyte concentration ranges are homologue dependent, with the lowest values for the tetrachlorinated dioxin and

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furan (0.5 pg/µL) and the highest values for the octachlorinated congeners (2000 pg/µL) (Table 2.).

B. Recovery Standard Solution - This nonane solution contains two recovery standards, $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD, at a nominal concentration of 100 pg/µL per compound. A 20 µL of this solution is spiked into each sample extract before the HRGC/HRMS analysis.

C. GC Column Performance/Retention Window Check Solution (RTCHK)- This solution contains the first and last eluting isomers for each homologous series from tetra- through heptachlorinated congeners. The solution also contains a series of closely eluting TCDD and TCDF isomers for the purpose of documenting the chromatographic resolution (Table 3).

D. Acceptance Criteria for Newly Prepared Standards - All components and concentrations of each calibration standard, recovery standard, internal standard, and matrix spike solutions are verified prior to use for the analysis of samples. Testing consists of back to back analysis of the "test" solution (the newly prepared solution) and a "control" solution (a known good solution). Control solutions are isolated from the production standards in a protected location. Both the control and test solutions are evaluated versus the current continuing calibration standard and versus each other. Each component of the test solution must be within 80 - 120% of the true concentration when calculated versus the control standard. The control standard must be within 80 - 120% of the true value when calculated versus the continuing calibration standard.

E. Standards are stored in 1/2 dram amber glass vials at room temperature.

V. SYSTEM PERFORMANCE CRITERIA

System performance criteria are presented below. It must be documented that all applicable system performance criteria specified in this Section are met before analysis for any sample is performed. Table 4 provides recommended GC conditions that can be used to satisfy the required criteria. During a typical 12-hour analysis sequence, the GC column performance and mass spectrometer resolving power checks must be performed at the beginning of the 12-hour period of operation. A routine calibration verification is required at the beginning and end of each 12-hour period during which samples are analyzed. A method blank or HRGC/HRMS solvent blank is required between a calibration run and the first sample run.

A. GC Column Performance

1. Inject the column performance check solution (Section IV. C.) and acquire selected-ion monitoring (SIM) data as described in Section III. E., III. F., and Table 4.

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2. The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers or between 2,3,7,8-TCDF and the peaks representing other TCDF isomers must be resolved with a valley of ≤ 25% (Fig. 1.), where:

   Valley Percent = (x/y) x 100

   x = height of valley measured between 2,3,7,8-TCDD or 2,3,7,8-TCDF and the closest TCDD or TCDF eluting isomers, and

   y = the peak height of 2,3,7,8-TCDD or 2,3,7,8-TCDF.

3. The acquisition time windows must be set to allow observation of the first and last eluting isomer of each congener. All first and last eluters of a homologous series should be labeled and identified on chromatograms.

B. Mass Spectrometer Performance

1. The mass spectrometer must be operated in the electron ionization mode. It is recommended that the ionization potential be set to optimize sensitivity for the given column flow and source design. A static resolving power of at least 10,000 (10% valley definition) must be demonstrated at appropriate masses before any analyses are performed. Static resolving power checks must be performed at the beginning and at the end of each 12-hour period of operation. It is recommended, however, that a check of the static resolution be made and documented by using the peak matching unit before and after each analysis. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

2. Chromatography time for PCDDs and PCDFs exceeds the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm can have serious adverse effects on instrument performance. Therefore, a mass-drift correction is mandatory. To that effect, use a lock-mass ion from the reference compound Perfluorokerosene (PFK) used for tuning the mass spectrometer and monitor and record the lock-mass ion channel during SIM acquisitions. The level of the reference compound (PFK) metered inside the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the selected lock-mass ion signal, regardless of the description number, does not exceed 10% of the full scale deflection for a given set of detector parameters. Under those

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conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

3. Using PFK molecular leak and an appropriate ion within the scan window, tune the instrument to meet the minimum required resolving power of 10,000 (10% valley).

   a) Documentation of the mass spectrometer resolving power is accomplished by recording the peak profile of the high-mass reference signal (m/z 416.9760) obtained during a peak matching experiment by using the low-mass PFK ion at m/z 330.9792 (or lower in mass) as a reference.

   b) The format of the peak profile representative allows manual determination of the peak resolution. The peak width (at 5% peak height) of the high-mass reference ion must not exceed 100 ppm (resolving power: 10,000). Peak width is determined by triangulation with no more than 10% allowance for sampling error. Instrumental ion transmission and resolution will be checked, adjusted and documented in case the resolution is below the minimum required 10,000 resolving power.

VI. CALIBRATION PROCEDURES:

A. Initial Calibration (ICAL)- Initial calibration of the instrument is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any continuing calibration does not meet the required criteria listed in Section VI. B..

1. All six calibration solutions listed in Table 2. must be used for the initial calibration.

2. Tune the instrument with PFK to achieve a static resolving power of at least 10,000 (10% valley) as described in section V. B..

3. Inject 2 µL of the GC column performance check solution and acquire SIM mass spectral data as described earlier in Section III. F. - G. Any further analysis must not be performed until it has been documented that the column performance criteria listed in section V. A. was met.

4. Using the same GC and MS conditions that produced acceptable results for the column performance check solution, analyze a 2 µL portion of each of the six calibration solutions with the following requirements.

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a) The ratio of integrated ion current for the ions appearing in Table 5 (homologous series quantitation ions) must be within the indicated control limits (set for each homologous series).

b) The ratio of integrated ion current for the ions belonging to the carbon-labeled internal, surrogate, alternate, and recovery standards must be within the control limits stipulated in Table 5.

NOTE: Ion ratios for all 17 native analytes and 18 carbon-labeled internal and recovery standards must be within the specified control limits simultaneously in one run for each of the six (6) calibration standard solutions. If the ion abundance ratios are outside the limits, corrective action must be taken and acceptable abundance ratios achieved before any samples may be analyzed.

c) For each SICP and for each GC signal representing the elution of a target analyte the signal-to-noise ratio (S/N) must be better than or equal to 10:1.

d) Referring to Table 6., calculate the 17 relative response factors (RRF) for unlabeled target analytes relative to their appropriate internal standards, according to the following formula:

$$RRF(n) = \frac{A_x \times Q_{is}}{Q_x \times A_{is}}$$

Where:

RRF(n)	=	Analyte RRF
A_x	=	sum of the integrated ion abundances of the quantitation ions (Table 1.) for unlabeled PCDDs/PCDFs,
A_{is}	=	sum of the integrated ion abundances of the quantitation ions (Table 1.) for the labeled internal standards,
Q_{is}	=	quantity of the internal standard injected (pg),
Q_x	=	quantity of the unlabeled PCDD/PCDF analyte injected (pg).

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The RRF(n) is a dimensionless quantity; the units used to express Q_{is} and Q_x must be the same.

e) Calculate the average analyte $\overline{RRF}$ and their respective percent relative standard deviations (%RSD) for the six calibration solutions.

$$\overline{RRF}_{(n)} = \frac{1}{6}\sum_{j=1}^{6} RRF_{(n)j}$$

Where n represents a particular PCDD/PCDF (2,3,7,8 substituted congener), and j is the injection number (or calibration solution number).

f) The relative response factors to be used for the determination of the concentration of total isomers in a homologous series are calculated as follows:

(1) For congeners that belong to a homologous series containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCDD, and TCDF), the mean RRF used will be the same as the mean RRF determined in Section V. A. 4. e).

NOTE: The calibration solutions do not contain $^{13}C_{12}$-OCDF as an internal standard. This is because a minimum resolving power of 12,000 is required to resolve the $[M+6]^+$ ion of $^{13}C_{12}$-OCDF from the $[M+2]^+$ ion of OCDD (and $[M+4]^+$ from $^{13}C_{12}$-OCDF with $[M]^+$ of OCDD). Therefore, the RRF for OCDF is calculated relative to $^{13}C_{12}$-OCDD.

(2) For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer (PeCDF - two, HxCDF - four, HxCDD - three, HpCDF - two) the mean RRF used for those homologous series will be the average of the mean RRFs calculated for all individual 2,3,7,8-substituted congeners.

NOTE: HRGC/HRMS responses of all isomers in a homologous series that do not have the 2,3,7,8-substitution pattern are assumed to be the same as the

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responses of one or more of the 2,3,7,8-substituted isomer(s) in that homologous series.

g) Referring to Table 7. and 8. calculate relative response factors (RRF) and average relative response factors (RRF) for internal, surrogate, and alternate standards relative to their appropriate recovery standards, according to the following formula:

$$RRF_{(m)} = \frac{A_s \times Q_{rs}}{Q_s \times A_{rs}}$$

$$\overline{RRF}_{(m)} = \frac{1}{6}\sum_{j=1}^{6} RRF_{(m)j}$$

Where:

m	=	congener type,
j	=	injection number,
A_s	=	sum of the integrated ion abundances of the quantitation ions for a given standard,
A_{rs}	=	sum of the integrated ion abundances of the quantitation ions for the appropriate recovery standard,
Q_{rs}, Q_s	=	quantities of, respectively, the recovery standard (rs) and a particular standard injected (pg),
$RRF_{(m)}$	=	relative response factor of a particular standard relative to an appropriate recovery standard, as determined from one injection, and
$\overline{RRF}_{(m)}$	=	calculated mean relative response factor of a particular labeled standard relative to an appropriate recovery standard, as determined from the six initial calibration injections.

5. Acceptance Criteria for Initial Calibration - The criteria listed below for acceptable calibration must be met before any analysis is performed.

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a) The percent relative standard deviations for the mean response factors from the 17 unlabeled standards must not exceed ± 20 percent, and those for the labeled reference compounds must not exceed ± 30%.

b) The S/N ratio for the GC signals present in every SICP (including the ones for the labeled standards) must be ≥ 10.

c) The isotopic ratios (Table 5.) must be within the specified control limits.

NOTE: If the criterion for acceptable calibration listed in Section VI. A. 5. a) is met, the analyte specific RRF can then be considered independent of the analyte quantity for the calibration concentration range. The mean RRFs will be used for all calculations until the continuing calibration criteria (Section VI. B.) are no longer met. At such time, new mean RRFs will be calculated from a new set of injections of the calibration solutions.

B. Continuing Calibration Check (CONCAL) - Continuing calibrations must be performed at the beginning of a 12 hour period after successful mass resolution and QC resolution performance checks. A continuing calibration is also required at the end of a 12 hour shift.

1. Inject 2 µL of the CONCAL solution HRCC-3 standard (Table 2). By using the same HRGC/HRMS conditions as described in Section V., and used to determine and document an acceptable calibration as provided in Section VI. A. 5..

2. Acceptance Criteria for Continuing Calibration - The following criteria must be met before further analysis is performed.

a) The measured RRFs for the unlabeled standards obtained during the continuing calibration runs must be within ± 20 percent of the mean values established during the initial calibration (Section VI. A. 4. e) and f)).

b) The measured RRFs for the labeled standards obtained during the routine calibration must be within ± 30 percent of the mean values established during the initial calibration (Section VI. A. 4. g)).

c) The ion-abundance ratios (Table 5.) must be within the allowed control limits.

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d) If either one of the criteria in Sections VI. B. 2. a) and b) is not satisfied, repeat one more time. If these criteria are still not satisfied, the entire continuing calibration process must be reviewed.

e) If the continuing calibration at the end of a 12-hour period fails no more than 25% RPD for the unlabeled compounds and 35% RPD for the labeled reference compounds, use the mean RRFs from the two daily calibration runs to compute analyte concentrations, instead of the RRFs obtained from the initial calibration.

NOTE: If RRFs for up to two labeled standards fail by more than 35%, the calibration is considered acceptable, as long as corresponding unlabeled analytes meet criteria.

f) Continuing calibrations analyzed at the end of the 12 hour period which fail by more than 25% RPD for the unlabeled compounds and 35% RPD for the labeled reference compounds must be documented according to the non-conformance SOP. The analyst must assess the effect of failure on overall data quality. The assessment will include evaluation of any spiked samples included in the 12 hour "clock", presence of reportable levels of the affected analytes in the samples, and sample data obtained during the period between beginning and ending calibrations. All samples which contain reportable levels of a "failed" analyte will be reanalyzed unless a passing spiked sample has been analyzed between the sample and the ending calibration standard.

VII. ANALYSIS

A. A valid analysis of column performance check, calibration and method or instrument blank must have been obtained prior to the analysis of any sample.

B. Remove the sample extract (blown to dryness) or blank from storage. Add 20 µL of recovery standard and mix thoroughly. Care must be taken to coat the walls of the vial several times to dissolve the sample material deposited on the walls during the concentration process.

NOTE: A final volume of 20 µL or more should be used whenever possible. A 10 µL final volume is difficult to handle, and injection of 2 µL out of 10 µL leaves little sample for confirmations and repeat injections, and for archiving.

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C. Inject a 2 µL aliquot of the extract into the GC, operated under the GC conditions that have produced acceptable CONCAL and RTCHK results.

D. Acquire SIM data using the same acquisition and mass spectrometer operating conditions previously used to determine the relative response factors.

NOTE: The acquisition period must at least encompass the PCDD/PCDF overall retention time window previously determined. Selected ion current profiles (SICP) for the lock-mass ions (one per mass descriptor) must also be recorded and included in the data package. These SICPs must be true representations of the evolution of the lock-mass ions amplitudes during the HRGC/HRMS run. The analyst may be required to monitor a PFK ion, not as a lock mass, but as a QC ion, in order to meet this requirement. It is recommended to examine the QC ion or lock-mass ion SICP for obvious basic sensitivity and stability changes of the instrument during the GC/MS run that could affect the measurements. Report any discrepancies in the case narrative.

E. Identification Criteria - For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

1. Retention Times

a) For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard present in the sample extract (this represents a total of 10 congeners including OCDD; Table 1.), the retention time (RRT; at maximum peak height) of the sample components (i.e., the two ions used for quantitation purposes listed in Table 1.), must be within -1 to +3 seconds of the isotopically labeled standard.

b) For 2,3,7,8-substituted compounds that do not have an isotopically labeled internal standard present in the sample extract (this represents a total of eight congeners; Table 1.), the retention time must fall within 0.005 retention time units of the relative retention times measured in the continuing calibration. Identification of OCDF is based on its retention time relative to $^{13}C_{12}$-OCDD as determined from the 12 hour continuing calibration results.

c) For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding homologous retention time windows established by analyzing the RTCHK solution.

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d) The ion current responses for both ions used in quantitation (e.g., for TCDDs: m/z 319.8965 and 321.8936) must reach maximum simultaneously (± 2 seconds).

e) The ion current responses for both ions used for the labeled standards (e.g., for $^{13}C_{12}$-TCDD: m/z 331.9368 and m/z 333.9339) must reach maximum simultaneously (± 2 seconds).

2. Ion Abundance Ratios

The integrated ion current for the two ions used for quantitation purposes must have a ratio between the lower and upper limits established for the homologous series to which the peak is assigned (Table 5.).

3. Signal-to-Noise (S/N) Ratio

All ion current intensities must be ≥ 2.5 times noise level for positive identification of a PCDD/PCDF compound or a group of coeluting isomers.

4. Polychlorinated Diphenyl Ether Interferences

In addition to the above criteria, the identification of a GC peak as a PCDF can only be made if no signal having a S/N ≥ 2.5 is detected, at the same retention time (± 2 seconds), in the corresponding polychlorinated diphenyl ether (PCDPE, Table 1.) channel or if the PCDPE signal is less than 10% of the PCDF signal.

F. Quantitation

1. For gas chromatographic peaks that have met specified criteria calculate the concentration of the PCDD or PCDF compounds using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \times \overline{RRF}_{(n)}}$$

Where:

C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g,

A_x = sum of the integrated ion abundances of the quantitation ions (Table 1.) for unlabeled PCDDs/PCDFs,

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A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 1.) for the labeled internal standards,

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

W = weight or volume, in grams or liters, of the sample (solid or liquid), and

$\overline{RRF}_{(n)}$ = calculated mean relative response factor for the analyte.

2. Calculate the percent recovery of the nine internal standards measured in the sample extract, using the formula:

$$\text{Internal Standard Recovery} = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times \overline{RRF}_{(m)}} \times 100$$

Where:

A_{is} = sum of the integrated ion abundances of the quantitation ions (Table 1.) for the labeled internal standard,

A_{rs} = sum of the integrated ion abundances of the quantitation ions (Table 1.) for the labeled recovery standard; the selection of the recovery standard depends on the type of congeners (Table 7.),

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

Q_{rs} = quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and

$\overline{RRF}_{(m)}$ = calculated mean relative response factor for the labeled internal standard relative to the appropriate (see Table 7) recovery standard.

3. Calculate the percent recovery of seven surrogate and alternate standards using expression VII. F. 2..

NOTE: For the air samples (PUF, M-0023A) calculate percent recovery of five surrogate standards relative to their appropriate internal standards.

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4. If the concentration in the final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compound exceeds the dynamic range of the instrument (i.e., saturation in a mass channel) then solvent will be added to the extract to bring the signal level into the instrument's dynamic range. Any dilutions must be pre-approved by the client.

5. The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of GC signals included in the homologous total concentration value must be specified in the report.

6. Sample Specific Estimated Detection Limit - The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, depending on the type of response produced during the analysis of a particular sample.

   a) Samples giving a response for at least one quantitation ion that is less than 2.5 times the background level.

      The area of the analyte is replaced by the noise level measured in a region of the chromatogram clear of genuine GC signals multiplied by an empirically determined factor. The detection limits represent the maximum possible concentration of a target analyte that could be present without being detected.

$$DL = \frac{2 \times 2.5 \times (F \times H) \times Q_{is}}{A_{is} \times \overline{RRF}_{(n)} \times W}$$

Where:

DL	=	estimated detection limit for a target analyte, expressed in ng or pg.
2.5	=	minimum signal/ noise required for a GC signal to be accepted.
F	=	an empirical number that approximates the area to height ratio for a GC signal. (F= 3.7 for all dioxin/ furan analyses.)

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H	=	height of the noise.
A_{is}	=	integrated current of the characteristic ions of the corresponding internal standard.
Q_{is}	=	amount of internal standard added to the sample before extraction.
$\overline{RRF}_{(n)}$	=	mean analyte relative response factor from the initial calibration.
W	=	sample weight or volume.
2	=	used to account for the two signals present for every analyte.

b) Samples characterized by a response above the background level with a S/N of at least 2.5 for both quantitation ions.

When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet ion ratio requirements (Table 5.) calculate the "Estimated Maximum Possible Concentration" (EMPC) according to the expression shown in Section VII. F. 1., except that A_x should represent the sum of the area under the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio.

VIII. QUALITY CONTROL REQUIREMENTS

A. GC column performance must be demonstrated initially and verified prior to analyzing any sample in a 12-hour period. The GC column performance check solution must be analyzed under the same chromatographic and mass spectrometric conditions used for other samples and standards.

B. Routine calibrations must be performed at the beginning of a 12-hour period after successful mass resolution and GC resolution performance checks and at the end of a 12-hour period following the analysis of samples.

C. The target detection limits will be the following:

1. TDLs for waters (sample size - 1L):

≤ 10 ppq	TCDD & TCDF
≤ 50 ppq	Penta - HeptaCDD & CDF
≤ 100 ppq	OCDD & OCDF

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2. TDLs for solids (sample size - 10g):

≤ 1 ppt	TCDD & TCDF
≤ 5 ppt	Penta - HeptaCDD & CDF
≤ 10 ppt	OCDD & OCDF

3. For air (e.g., PUF, M-0023A) or Wipes (sample size - 1):

≤ 50 pg	TCDD & TCDF
≤ 250 pg	Penta - HeptaCDD & CDF
≤ 500 pg	OCDD & OCDF

D. Method Blank

1. Percent recoveries of all labeled standards should be between 40 - 135%. Method blank with standard recoveries below 40% (but ≥ 25%) is acceptable as long as signal to noise for affected standards is ≥ 10:1.
2. Target detection limits must be met for each analyte. (VIII. C.)
3. No reportable analytes should be present in the Method Blank. Up to 3 analytes may be present at levels below 1/2 Target Detection Limit (TDL) as long as the compounds were not reported in the previous analysis.
4. For Method Blanks associated with high level samples, the analyte level in the blank must be < 5% of the quantity present in the samples.

E. LCS/ LCSD and MS/ MSD

1. Percent recoveries of all labeled standards should be between 40 - 135%. LCS/ LCSD or MS/ MSD with labeled standard recoveries below 40% (but ≥ 25%) are acceptable as long as signal to noise for affected standards is ≥ 10:1.
2. Percent recoveries of all analytes should be between 70 - 130%. For up to two analytes, recoveries may be as high as 145% or as low as 60%, as long as the associated relative percent differences (%RPDs) meet criteria.
3. Relative percent difference between LCS and LCSD or MS and MSD should be ≤ 20% for all analytes. For up to two analytes, %RPDs may be higher (up to 35%), as long as the associated percent recoveries meet criteria.

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F. Samples

1. Percent recoveries of all labeled standards should be between 40 - 135%. Samples with standard recoveries below 40% (but ≥ 25%) are acceptable as long as signal to noise for affected standards is ≥ 10:1. In the case of OCDD internal standards, the OCDF analyte must be below TDL also.

2. Specific detection limits must not exceed the target detection limits unless prohibited by a limited sample size or the need for dilution.

3. If the method blank contains reportable analytes but those analytes are not detected in the sample, the sample data may be reported.

4. Samples which fail acceptance criteria listed above (VIII. F. 1. and 2.) or associated with failing method blank or LCS/ LCSD (VIII. D. 1. - 4.; VIII. E. 1. - 3.) must be reextracted and reanalyzed. Exceptions may be made for sample matrices which require extreme additional cleanup procedures.

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TABLE 1: ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HRGC/HRMS FOR PCDDs AND PCDFs

Descriptor Number[b]	Accurate Mass[a]	Ion Type	Elemental Composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$13C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)

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TABLE 1 CONTINUED

Descriptor Number[b]	Accurate Mass[a]	Ion Type	Elemental Composition	Analyte
3 Continued	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$13C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{13}	PFK
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCDPE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)

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TABLE 1 CONTINUED

Descriptor Number[b]	Accurate Mass[a]	Ion Type	Elemental Composition	Analyte
4 Continued	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

a) The following nuclidic masses were used:

H = 1.007825
C = 12.000000
^{13}C = 13.003355
F = 18.9984
O = 15.994915
^{35}Cl = 34.968853
^{37}Cl = 36.965903

S = Labeled Standard
QC = Ion Selected for Monitoring the Instrument Stability During the GC/MS Analysis

b) Descriptor 1 contains mono-, di- and trichlorinated dibenzodioxins and dibenzofurans that are not quantitated by Method 8290.

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TABLE 2: COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL) Sol. Number: 1	2	3	4	5	6
Unlabeled Analytes						
2,3,7,8-TCDD	0.5	1	10	50	100	200
2,3,7,8-TCDF	0.5	1	10	50	100	200
1,2,3,7,8-PeCDD	2.5	5	50	250	500	1000
1,2,3,7,8-PeCDF	2.5	5	50	250	500	1000
2,3,4,7,8-PeCDF	2.5	5	50	250	500	1000
1,2,3,4,7,8-HxCDD	2.5	5	50	250	500	1000
1,2,3,6,7,8-HxCDD	2.5	5	50	250	500	1000
1,2,3,7,8,9-HxCDD	2.5	5	50	250	500	1000
1,2,3,4,7,8-HxCDF	2.5	5	50	250	500	1000
1,2,3,6,7,8-HxCDF	2.5	5	50	250	500	1000
1,2,3,7,8,9-HxCDF	2.5	5	50	250	500	1000
2,3,4,6,7,8-HxCDF	2.5	5	50	250	500	1000
1,2,3,4,6,7,8-HpCDD	2.5	5	50	250	500	1000
1,2,3,4,6,7,8-HpCDF	2.5	5	50	250	500	1000
1,2,3,4,7,8,9-HpCDF	2.5	5	50	250	500	1000
OCDD	5	10	100	500	1000	2000
OCDF	5	10	100	500	1000	2000
Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	100

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PCDDs AND PCDFs BY HRGC/HRMS - METHOD 8290	
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TABLE 2 CONTINUED

Compound	Concentrations (pg/µL) Sol. Number: 1	2	3	4	5	6
Internal Standards Continued						
$^{13}C_{12}$-OCDD	200	200	200	200	200	200
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	100
Surrogate Standards						
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	1	10	50	100	200
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	100
Alternate Standard						
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100	100
Recovery Standards						
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	100

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PCDDs AND PCDFs BY HRGC/HRMS - METHOD 8290	
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TABLE 3: GC RETENTION TIME WINDOW DEFINING SOLUTION AND ISOMER SPECIFICITY TEST STANDARD (SECTION IV. C.)

DB-5 COLUMN GC RETENTION TIME WINDOW DEFINING SOLUTION

CDD/ CDF	FIRST ELUTED	LAST ELUTED
TCDF	1,3,6,8	1,2,8,9
TCDD	1,3,6,8	1,2,8,9
PeCDF	1,3,4,6,8	1,2,3,8,9
PeCDD	1,2,4,7,9	1,2,3,8,9
HxCDF	1,2,3,4,6,8	1,2,3,4,8,9
HxCDD	1,2,4,6,7,9	1,2,3,4,6,7
HpCDF	1,2,3,4,6,7,8	1,2,3,4,7,8,9
HpCDD	1,2,3,4,6,7,9	1,2,3,4,6,7,8

DB-5 COLUMN TCDD SPECIFICITY TEST STANDARD

1,2,3,7 + 1,2,3,8 - TCDD
2,3,7,8 - TCDD
1,2,3,9 - TCDD

DB-225 COLUMN TCDF ISOMER SPECIFICTY TEST STANDARD

2,3,4,7 - TCDF
2,3,7,8 - TCDF
1,2,3,9 - TCDF

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TABLE 4: GAS CHROMATOGRAPHY CONDITIONS

Column type	**DB-5**	**DB-225**
Length (m)	60	30
i.d. (mm)	0.25	0.25
Film Thickness (um)	0.25	0.25
Carrier Gas	Helium	Helium
Carrier Gas Flow (mL/min)	1-2	1-2
Injection Mode	⇐ splitless ⇒	
Valve Time (s)	60	60
Initial Temperature (°C)	150	130
Injection Port Temperature (°C)	250	250
Program Temperature	⇐ See Note ⇒	

Note: The GC temperature program is subject to change. Refer to work area guidelines for exact definitions of the current run conditions and descriptor name.

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TABLE 5. ION-ABUNDANCE RATIO ACCEPTABLE RANGES FOR PCDDs AND PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6a	M/M+2	0.51	0.43	0.59
7b	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

a) Used only for ^{13}C-HxCDF
b) Used only for ^{13}C-HpCDF

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TABLE 6. UNLABELED ANALYTES QUANTITATION RELATIONSHIPS

Analyte	Standard Used During Quantitation
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
Other TCDDs	$^{13}C_{12}$-2,3,7,8-TCDD
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD
Other PeCDDs	$^{13}C_{12}$-1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
Other HxCDDs	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
Other HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
OCDD	$^{13}C_{12}$-OCDD
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF
Other TCDFs	$^{13}C_{12}$-2,3,7,8-TCDF
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
Other PeCDFs	$^{13}C_{12}$-1,2,3,7,8-PeCDF
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF

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TABLE 6 CONTINUED

Analyte	Standard Used During Quantitation
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
Other HxCDFs	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
Other HpCDFs	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
OCDF	$^{13}C_{12}$-OCDD

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TABLE 7: INTERNAL STANDARDS QUANTITATION RELATIONSHIPS

Internal Standard	Standard Used During Percent Recovery Determination
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

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TABLE 8: SURROGATE/ALTERNATE STANDARDS QUANTITATION RELATIONSHIPS

Surrogate/Alternate/Cleanup Standard	Standard Used During Percent Recovery Determination
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	13C_{12}-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

NOTE : For air samples (PUF and M-0023A) recoveries of surrogate standards are quantitated relative to their appropriate internal standards.

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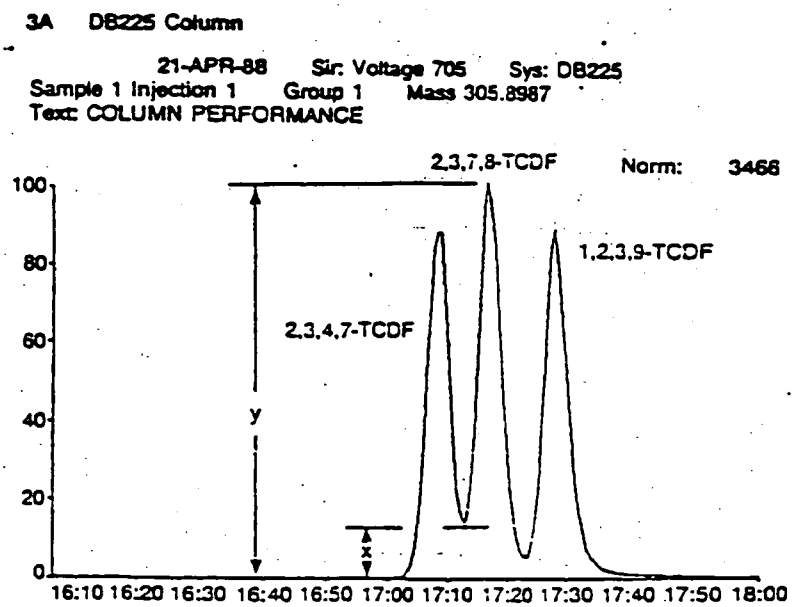

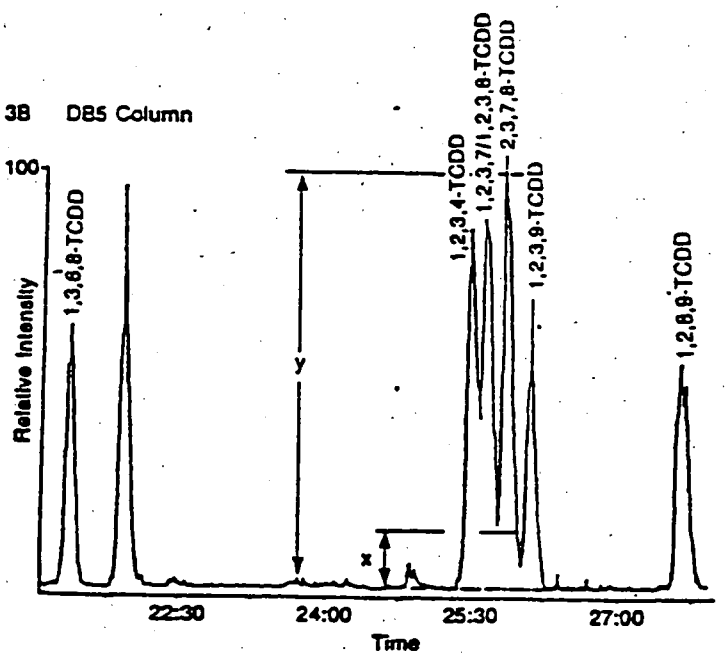

FIGURE 1. Valley between 2,3,7,8 - Tetra Dioxin and Furan Isomers and Other Closely Eluted Isomers.

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APPENDIX 1

Deviations from and improvements to US EPA Method 8290
POLYCHLORINATED DIBENZODIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs) BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/ HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/ HRMS)
as performed at Triangle Laboratories, Inc.

See Section	
• IV. A. and Table 2.	Triangle Laboratories uses 6 calibration points ranging from 0.5 pg/µL to 200 pg/µL for tetrachlorinated dioxin and furan. Concentrations of penta- through heptachlorinated analytes are 5 times higher than tetra congeners and octachlorinated analytes are 10 times higher (Compare with Table 5., Method 8290).
• IV. A.	Seven more labeled PCDDs/ PCDFs are used as surrogate and alternate standards to provide additional quality control information.
• IV. A.	The 1,2,3,6,7,8 - hexachlorodibenzofuran (HxCDF) is used as an internal standard instead of 1,2,3,4,7,8 - HxCDF. Triangle Laboratories uses 1,2,3,4,7,8 - HxCDF as a surrogate standard.
• IV. A.	Each carbon-labeled standard in the initial calibration solution has a concentration of 100 pg/µL except $^{13}C_{12}$ - OCDD, which is at 200 pg/µL. Concentrations of $^{13}C_{12}$ - labeled standards in sample fortification solutions are the same as in the initial calibration solution (See section 5.9., Method 8290).
• V.	The method blank does not need to be analyzed on each analysis clock that samples are analyzed. Once a valid analysis is provided for the method blank it may be replaced with HRGC/ HRMS solvent blank (See section 8.2., Method 8290).
• V. B. 3. a)	Documentation of the mass spectrometer resolving power is accomplished by recording the peak profile of m/z 416.9760 and 330.9792 (See section 8.2.2.3., Method 8290).
• VII. F. 6. a)	To calculate the sample specific Estimated Detection Limit, noise equivalent area is used instead of noise height (See section 7.9.5.1.1., Method 8290).
• VIII. D. - F. 1.	The Internal Standard recoveries in all QC samples and field samples are considered valid as long as the signal to noise ratio is greater than 10:1, the recovery is $\geq$ 25% and target detection limits for the analytes are met (See section 8.4., Method 8290).
• VIII. E. 2.	For up to two analytes in LCS/ LCSD and MS/ MSD, recoveries may be as high as 145% or as low as 60%, as long as the associated relative percent differences (%RPDs) meet criteria.

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PCDDs AND PCDFs BY HRGC/HRMS - METHOD 8290	
TLI SOP No DHR182 Version: 6	Date Written: February 9, 1998

APPENDIX 1 Continued

- VIII. E. 3. For up to two analytes in LCS/ LCSD and MS/ MSD, %RPDs may be higher (up to 35%), as long as the associated percent recoveries meet criteria.

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DATA PACKAGE ASSEMBLY AND SHIPPING

TLI SOP No. DPA104	Version: 12	Effective Date:	11/30/98
Author:	David Chu	Date Written:	October 1, 1998
Authorization: Phil Albro Management		Date Authorized:	11/20/98

I. **SCOPE AND APPLICATION:** The purpose of this SOP is to describe the procedures to follow when assembling and shipping all data packages at Triangle Laboratories, Inc. The deliverables of the standard data package contain an identification document stating that Triangle Laboratories, Inc. produced the results.

II. **PROCEDURE:**

A. Assemble the data package, including: the address documentation, the signed case narrative, Triangle Labs list of certifications, document control or project description section, all Sample Data Summary sheets with chromatograms and calibration data for each project. Paginate everything that is going to the client. Go to the last page of the Case Narrative and, in the space provided, enter the total number of pages in the document. Unless the client has requested otherwise, send them the original case narrative and the copy of other deliverables.

NOTE: To obtain the address documentation, go into MILES and Select "F", enter project number, printout destination, Select "M" for Marked for shipment. If it is to be shipped out the door, then type "Y" for transfer to archive. If not, type "N".

B. For high resolution data packages only, locate all calibration data pertaining to the project. Refer to the Reporting Option located in the Reporting Requirements of the Sample Tracking and Project Management Form. Copy only summary sheets for CONCALs and ICALs to send to customer. Some clients request full calibration data which includes summary data sheets and chromatograms for CONCALs, ICALs and retchecks. Calibration data for all other projects should be furnished.

C. Before copying data package, go to the MILES system. At the main menu, select "F" for Shipping/Archiving. On Shipping/Archiving Information Sub-menu, select "Sample shipment Update/Inquiry."

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DATA PACKAGE ASSEMBLY AND SHIPPING					
TLI SOP No.	DPA104	Version:	12	Date Written:	October 1, 1998

D. Enter project number, extension (if applicable) and "M" for marked for shipment, "T" for transfer to archive. Also enter password for this screen.

E. The samples for this project will appear on the screen. The project must be in shipping (D-SH, O-SH, I-SH, S-SH) in order to perform this function. If not, go back to the shipping sub-menu and select option "Production By Project and/or Worklist." Transfer project to shipping.

F. All samples for project will be tagged if project is in shipping. Press <F10> to transfer shipping information to accounting. The computer will issue a printout with all the shipping information including price, address, and special instructions.

G. Follow all instructions closely. Copy data packages according to instructions listed on the printout.

H. The computer will automatically archive all projects if you indicate it to do so by typing "Y".

I. See SOP on shipping projects.

NOTE: When copying BNA projects, set the copier on 93% reduction to avoid chopping off the interim.

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EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613, 8290 AND 551

TLI SOP No. DSP161	Version: 16	Effective Date:	October 23, 1998
Author:	Phil Albro	Date Written:	October 2, 1998
Authorization: Phil Albro (Management)		Date Authorized:	10/18/98

I. **SCOPE AND APPLICATION:** This SOP provides procedures for the extraction of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD and PCDF) from water samples in accordance with methods 1613 or 8290. It may also be applied to the extraction of tetrachlorodibenzo-p-dioxins and tetrachlorodibenzofuran from water in accordance with method 551. See the SOP on Preparation for Extraction of PCDD/PCDF from Water before using the present SOP.

II. **SAFETY CONSIDERATIONS:** Samples may contain harmful substances. Wear labcoat, appropriate eyewear, and gloves. These solvents are flammable; avoid flames and sparks. Do not breathe the vapors, and avoid contact with skin and eyes. They may cause irritation, nausea, dizziness, and, in extreme cases, death. For additional safety and health information, see the TLI Safety and Health Manual and the appropriate MSDS.

III. **REAGENTS:**

A. Organic-free reagent water- Either Dracor or Fisher HPLC Grade

B. Heptane-pesticide grade or better quality, less than 1 ppm residue on evaporation.

C. Sodium sulfate-anhydrous, pesticide grade.

D. Methylene Chloride-pesticide grade or better quality.

E. Toluene-pesticide grade or better quality.

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IV. GLASSWARE PREPARATION:

A. All glassware used in this procedure must have been prepared according to the SOP entitled "Glassware Cleaning".

B. The following glassware is needed for each sample:

2 L separatory funnel with stopper and Teflon© stopcock

A. 1000 mL graduated cylinder

medium glass powder funnel

250 mL round bottom flask

500 mL extraction flask and regular thimble holder (pre-Soxlet extracted).

Soxlet extractor (pre-Soxlet extracted).

Soxhlet Dean-Stark (SDS) extractor - pre-soxhlet extracted and ready for use

A. Assemble the separatory funnel(s) with stopcock and stopper.

B. Rinse the following with heptane:

separatory funnel(s)

graduated cylinder(s)

all flasks

glass powder funnel(s)

A. While rinsing the separatory funnel(s), close the stopcock and check for leaks. Drain the funnel into a waste container.

B. After rinsing, invert all flasks and allow to fully drain.

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C. Plug the powder funnel(s) with pre-cleaned glasswool. Fill the powder funnel 3/4 full with anhydrous sodium sulfate.

I. **SEPARATORY FUNNEL EXTRACTION PROCEDURE:**

A. If has not already been done in the preparation of the sample for extraction, pour the sample volume into a 2 L separatory funnel. Rinse the sample bottle with 60 mL of methylene chloride and transfer to the separatory funnel.

B. Extract the aqueous phase with methylene chloride as follows:

1. Shake the separatory funnel with water sample and methylene chloride for 5 minutes using Glas-Col Automatic Shaker (or 2 minutes by hand). Be sure to vent the funnel periodically to avoid pressure buildup.

   Note: If using the Gas-Col shaker, set the timer for 5 minutes and turn the power on. Slowly increase the speed to 40 or the maximum speed possible without displacing any sample through the vent.

   Allow the solvent layers to settle for 10 minutes. If emulsions occur, filter the water + emulsion through a G8 filter or glass wool with a methylene chloride rinse. Add the methylene chloride rinses to the methylene chloride extract.

2. Drain the methylene chloride layer through anhydrous sodium sulfate into a 250 mL flask.

3. Repeat steps 1-3 two more times using 60 mL methylene chloride for each extraction. A total of three extractions are required for each sample.

1. Rinse the sodium sulfate twice with 10 mL methylene chloride. Collect the methylene chloride rinses in the 250 mL flask containing the sample extract.

I. **EXTRACTING THE FILTER:**

A. Soxhlet extract the filters, glasswool used to break emulsions, and all filtered solids as follows:

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1. Place filters in a toluene pre-Soxhlet extracted thimble (500 mL size).

2. For methods 1613 and 8290, add 375-400 mL of toluene to the 500 mL boiling flask; For method 551, use 400 mL of ethanol: toluene 68:32 (v/v) to the 500 mL flask.

3. Add 5-6 Teflon boiling chips to the boiling flask.

4. Place the label containing information for the concentration process on the boiling flask on top of colored lab tape. Write solvent used on flask with marker.

   a) Do not place set up on hotplates until extraction of the water phase is completed to insure no additional emulsions need to be filtered and the filter or glasswool placed into the thimble with the first filter.

2. Extract using pre-Soxhlet extracted Soxhlet apparatus for 16 hours.

3. After extraction, let cool and ensure the label indicating that this extract is to be combined with the methylene chloride extract from the water phase is still intact.

II. CONTINUOUS LIQUID-LIQUID EXTRACTION PROCEDURE:

Note: The use of the continuous liquid-liquid extractor is always allowed as an alternative to separatory funnel extraction in method 8290. It is the technique of choice when a given sample type is known to produce difficult emulsions. Use this technique with methods 1613 (A or B) and 551 whenever a re-extraction is needed because of low recoveries during the separatory funnel extraction step. Be sure to indicate on the extraction form whenever L-L extraction was used.

Note 2: The L-L extractor simply substitutes for a separatory funnel; therefore all considerations of filtering, determination of solids or particulate solids, or water vs. sludge described in the SOP on Preparation for Extraction of PCDD/PCDF from Water for Methods 1613, 8290 and 551 still apply.

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EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613A 8290 AND 551	
TLI SOP No. DSP161 Version: 16	Date Written: October 2, 1998

A. Assemble Glassware

1. Using pre-extracted glassware, rinse the extractor body and 500 mL flat bottom flask with methylene chloride. Discard rinse as waste.

2. Place 5-6 methylene chloride pre-extracted boiling chips in the flat bottom flask. Add approximately 250 mL of clean methylene chloride to the flask.

3. Add approximately 150 mL of methylene chloride to the extractor body.

4. Attach extractor body to the flask with green plastic clamp.

5. Label flat bottom with solvent, project number and sample number using color labels.

B. Preparation of Water Sample

1. Measure and record 1 liter of Reagent water each for blank and either OPR (1613), or LCS/LCSD (8290) utilizing a 1000 mL graduated cylinder.

2. Measure 1000 mL of well mixed sample and transfer to the extractor body. Record this volume on the sample preparation and tracking form. Note: If the sample does not contain 1000 mL, record the volume it does contain, but make up the difference with Reagent water. The L-L apparatus needs 1000 mL of water to operate correctly. The sample size to use in calculations, however, is the actual sample size not including make-up water.

3. Rinse the 1000 mL graduated cylinder three times with 20 mL methylene chloride and transfer rinses to the extractor body.

C. Extraction

1. Place Continuous Liquid-Liquid setup on condenser/hot plate and seat securely in place. Use aluminum foil shimmies to align body vertically and to fill any space between hotplate and bottom of the flask.

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2. Turn hotplate on to 400 degrees.
3. Extract for 18 hours.
4. Dismantle setup after they have cooled. Keep only the methylene chloride in the flat bottom flask.
5. Discard water and methylene chloride in extractor body as waste.

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EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290

TLI SOP No. DSP105	Version: 15	Effective Date:	July 31, 1998
Author:	Don Harvan	Date Written:	May 4, 1998
Authorization: Phil Albro Management		Date Authorized:	5/27/98

I. **SCOPE AND APPLICATION:** This method provides procedures for the extraction of polychlorinated dibenzo-p-dioxin (tetra- through octachlorinated homologues; PCDDs) and polychlorinated dibenzofuran (tetra- through octachlorinated homologues; PCDFs) from non-tissue solids, including but not limited to soil, sediment, pulp, sludge, paper and/or cardboard, according to SW-846 Method 8290. Only the extraction procedure is contained in this SOP.

II. **SAFETY CONSIDERATIONS:** Samples may contain harmful substances. Wear labcoat, appropriate eyewear and gloves. Toluene and ethanol are flammable; avoid flames and sparks. The procedure has been validated for either heptane or hexane, since heptane is much less of a health hazard, it should be used instead of hexane whenever possible, but hexane can be used if heptane is unavailable. Do not breathe the vapors, and avoid contact with skin or eyes, as these solvents may cause irritation, nausea, and dizziness. For additional safety information, see the TLI Safety and Health Manual and the appropriate MSDS.

NOTES: **Slight procedural differences exist for specified sample types in this SOP. Be careful not to overlook these differences.**

III. **REAGENTS:**

A. Heptane- pesticide grade (< 1 ppm residue)

B. Toluene- pesticide grade (< 1 ppm residue)

C. Ethanol- OmnySolve grade

D. Ethanol/toluene (68/32 v/v) - Take 68 parts (by volume) of Ethanol and mix well with 32 parts (by volume) of Toluene.

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IV. GLASSWARE PREPARATION

A. All glassware used in this procedure must have been prepared according to glassware washing SOP.

B. The following glassware is needed for each sample:

1. beaker
2. 500 mL or 250 mL flat bottom flask
3. forceps
4. spatula
5. thimble holder - pre-Soxhlet extracted and ready to use
6. Soxhlet extractor - pre-Soxhlet extracted and ready to use

C. If wet sample ≥ 15 g, Soxhlet Dean Stark (SDS) extractor must be used in addition to the Soxhlet extractor. Be sure the SDS extractor has been pre-Soxhlet extracted.

D. The flask, thimble holder and Soxhlet or SDS extractor may be 250 or 500 mL, but all pieces must be the same size!

E. If SDS is required, assemble the SDS extractor with stopcock.

F. Rinse all glassware with n-heptane.

G. Label each beaker and flask by placing a color coded sample label on top of a strip of colored lab tape. The colored lab tape is necessary because the adhesive on the color coded labels is difficult to remove from the glass and will cause contamination problems.

H. All flasks require two labels - one on the side of the flask and one on the neck.

V. EXTRACTION PROCEDURE:

A. Plan the extraction batch. An extraction batch can contain up to twenty (20) samples and must include a method blank, a spike pair, and at least one(1) Lab

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Control Spike (LCS). Complete the QC batch form, including all samples and QC samples in the extraction batch.

B. Observe and document the physical appearance and consistency of each sample in the wet lab observation log in MILES.

C. Using the percent moisture analysis, determine the amount of sample necessary for a 10 g dry weight sample.

Note: Mix the sample well before taking an aliquot for extraction.

D. For each sample, weigh the amount of sample determined in step VI.C. above. Record the sample weight on the Sample Preparation Management and Tracking Form (SPMFT).

E. Make sure homogeneity is maintained--exclude anything that does not constitute sample's natural matrix.

F. Clean balance by swiping with heptane.

G. Zero balance. Weigh sample and its container.

H. Record the gross weight on the STMF (Sample Tracking and Management Form).

I. Tare beaker in which sample is to be transferred.

J. Record the sample weight on the STMF (Sample Tracking and Management Form). Also indicate with the letter"Y" or "N" if all the sample was used.

(Y)=There is enough sample left to perform re-extraction
(N)=There is NOT enough sample left to perform re-extraction

K. Reweigh sample and its container weight. Record the post-gross weight.

L. Prepare the blank using pre-extracted G-8 filters for pulps and all dried and ground samples. Prepare the blank using pre-extracted sand for all normal ash/sediment/soil/sludge samples. If any laboratory control samples (LCS and/or

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LCSD) are included in the batch, use the same matrix as Blank. Weigh out 10 grams (± 0.4) for each blank and/or OPR prepared.

M. Check the volume of each standard solution relative to the last volume mark. The bottom of the meniscus must be at the mark.

N. Spike all samples with 20 µL USF-I (0.1µg/mL). Spike any Lab Control Spikes,(LCS/LCSD), Matrix Spikes (MS/MSD) with 40 µL USF-MX (0.01 µg/mL). Record the volume, lot number, concentration and expiration date of each standard on the SPMFT and initial and date the entry. At the end of the spiking process, mark the bottom of the meniscus with a fine point permanent marking pen. Return the standard vials to the storage drawer.

Note: Dioxin standards must be stored at room temperature in amber, glass vials, with Teflon lined septa caps. Spiking instructions can be found in See SOP on Concentration of Extracts Using Rotary Evaporator.

O. After spiking place a glass wool plug on top of the sample in each thimble. Use pre-extracted glasswool.

P. Prepare the Soxhlet apparatus by:

1. Use a 500 mL setup, place 400 mL toluene* in the flatbottom flask. Add 5-6 Teflon boiling chips in each flask.
2. Place the label containing information for the concentration process on the boiling flask on top of the colored lab tape. Write the solvent used on the flask.
3. Place the pre-Soxhleted thimble holder on top of the flask.

Q. ***NOTE:** GP pulp sludge samples require 68:32 ethanol/toluene instead of toluene. GP pulp samples require ethanol instead of toluene. The volume remains 400 mL for 500 mL setup.

R. Place the thimble with the spike sample into the thimble holder. Be sure to seat the thimble at the bottom of the holder.

S. **NOTE:** While the Soxhlet apparatus is sitting on the counter, keep the top capped with aluminum foil to avoid contamination.

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T. Place the Soxhlet on top of the thimble holder. If Soxhlet Dean Stark (SDS) is being used, be sure the stopcock is closed.

U. Place the Soxhlet apparatus on the heating mantle and connect the Soxhlet apparatus to the condenser at the ground glass joint. Cap the top of the condenser with aluminum foil.

V. Wrap the thimble holder and Soxhlet extractor with foil. Do not cover the condenser.

W. **NOTE:** If using ethanol as the sole solvent, do not wrap any of the apparatus with aluminum foil.

X. Place a piece of colored tape on the condenser to indicate it is being used for a sample and needs to be pre-Soxhlet extracted after the sample extraction is completed.

Y. If the samples have been designated **high level** write **2X** on the tape. If samples have designated **Isolation** write **3X** on the tape.

Z. Turn on the heat. If using a hot plate, use the heat setting #5. If using a six (6) place mantle, use the HIGH setting.

AA. Check the units after one (1) hour. Each unit should be cycling at a rate of five (5) times per hour, have no leaks and have sufficient solvent. Open the aluminum foil on the thimble holder to check the cycling action and close the wrapping. Make adjustments as necessary.

BB. If adjustments were required, check the units again in one (1) hour. Otherwise check again in six (6) hours.

CC. If the weighed sample is >30g, drain the water from the SDS halfway through the extraction (i.e., approximately 8 hours after turning on the heaters).

DD. Extract the sample for 16 hours.

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TRIANGLE LABORATORIES, INC.
CONFIDENTIAL and PROPRIETARY INFORMATION

EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290

TLI SOP No. DSP105	Version: 15	Date Written: May 4, 1998

TRIANGLE LABORATORIES, INC.
Dioxin Sample Preparation Tracking & Management Form

PAGE 1 OF 1

Project: 91500

Client: Triangle Laboratories, Inc. (TLI01)

Solvent(s)/Acid(s): _____ / _____ / _____

Lot Numbers: _____ / _____ / _____

Method: 8290X:Tetra-octa Matrix: _____

Extraction Date: __/__/__

IS Spike: 20 µl conc: 0.1000 ng/µl

SS Spike: ___ µl conc: __.___ ng/µl

MS Spike: 0 µl conc: 0.0000 ng/µl

LCS Spike: 0 µl conc: 0.0000 ng/µl

						_____	_____	_____	_____	Chemist
						_____	_____	_____	_____	Spike #
						_____	_____	_____	_____	* ID
						__/__/__	__/__/__	__/__/__	__/__/__	* Expir
						__/__/__	__/__/__	__/__/__	__/__/__	* Date
						__:__	__:__	__:__	__:__	* Time
						_____ng/µl	_____ng/µl	_____ng/µl	_____ng/µl	* Conc.
						_____ µl	_____ µl	_____ µl	_____ µl	* Vol.
SS.crd	TLI SAMPLE ID	/ CLIENT SAMPLE ID	GROSS WEIGHT Before	GROSS WEIGHT After	SAMPLE SIZE g / ml					
000	TLI Blank	TLI Method Blank								Any Left: yes/no
										Any Left: yes/no
										Any Left: yes/no
										Any Left: yes/no
										Any Left: yes/no
										Any Left: yes/no
										Any Left: yes/no
										Any Left: yes/no
										Any Left: yes/no
										Any Left: yes/no

Gross weight of sample container - sample before/after aliquot removal.

Comments: _____

_____

_____

_____ Initials: _____ Date: __/__/__

Initials of both SPIKER AND CHEMIST must be entered.

XXXXX - Gross Weight not provided for WATER Samples.

REV 05/27/97 (PSTMF 71)

ATTACHMENT 1

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EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
TLI SOP No. DSP105 Version: 15	Date Written: May 4, 1998

Composition of Fortification Standards

USF-I

Analyte	Concentration (µg/mL)
13C, 2,3,7,8-TCDF	0.1
13C, 2,3,7,8-TCDD	0.1
13C, 1,2,3,7,8-PeCDF	0.1
13C, 1,2,3,7,8-PeCDD	0.1
13C, 1,2,3,6,7,8-HxCDF	0.1
13C, 1,2,3,6,7,8-HxCDD	0.1
13C, 1,2,3,4,6,7,8-HpCDF	0.1
13C, 1,2,3,4,6,7,8-HpCDD	0.1
13C-OCDD	0.2

USF-MX

	Concentration (µg/mL)
3-MonoCDF	0.01
3-MonoCDD	0.01
2,3-DiCDF	0.01
2,3-DiCDD	0.01
2,3,8-TriCDF	0.01
1,2,4-TriCDD	0.01
2,3,7,8-TCDF	0.01
2,3,7,8-TCDD	0.01
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.05
1,2,3,7,8-PeCDD	0.05
1,2,3,4,7,8-HxCDF	0.05
1,2,3,6,7,8-HxCDF	0.05
1,2,3,7,8,9-HxCDF	0.05
2,3,4,6,7,8-HxCDF	0.05
1,2,3,4,7,8-HxCDD	0.05
1,2,3,6,7,8-HxCDD	0.05
1,2,3,7,8,9-HxCDD	0.05
1,2,3,4,6,7,8-HpCDF	0.05
1,2,3,4,7,8,9-HpCDF	0.05
1,2,3,4,6,7,8-HpCDD	0.05
OCDF	0.1
OCDD	0.1

USF-C

Analyte	Concentration (µg/mL)
37Cl- 2,3,7,8-TCDD	0.01

ATTACHMENT 2

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SOP DSP 260 IS CONSIDERED TO BE CONFIDENTIAL AND PROPRIETARY. THEREFORE, THIS SOP DOES NOT APPEAR IN THIS ADDENDIX. THIS SOP HAS BEEN SUBMITTED TO EPA UNDER CTO 038 FOR NSWC CRANE.

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CREATING THE TLI CHAIN OF CUSTODY

TLI SOP No. SMC114	Version: 2	Effective Date:	March 1, 1996
Author:	Bill Hurst	Date Written:	January 16, 1996
Technical Approval:	Sample Prep WGL	Date Approved:	2-22-96
Authorization:	Sarah VanOlson	Date Authorized:	2/26/96

I. **SCOPE AND APPLICATION:** The purpose of this SOP is to describe the procedure to be followed when creating the TLI Chain of Custody (COC).

II. **RESPONSIBILITY:** It is the responsibility of the Sample Custodian or designated assistant to create the C.O.C..

III. **PROCEDURE:**

A. The TLI COC is an automated document generated within the MILES System whenever any new project is entered into the system (see page 3.)

B. To generate the TLI COC from the Main Menu within the MILES System select option A.

C. To print the TLI COC select option C from the Project Initiation and Maintenance Menu.

NOTE: Be sure your printer is set to print in the condensed mode.

D. Type in the project number and select option R.

E. The following items are selected in the MILES System and automatically printed onto the C.O.C.:

1. custody seal
2. chain of custody
3. sample tags
4. sample tag numbers

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CREATING THE TLI CHAIN OF CUSTODY	
TLI SOP No. SMC114 Version: 2	Date Written: January 16, 1996

5. SMO form
6. type of container used in shipping process, for example: ice chest, styro cooler, etc
7. type of cooling agent used in shipping process, for example: dry ice, ice, ambient recorded temperature

F. The originator's signature must be included on each page of the TLI COC.

G. Please fill in the following in the Receiving Remarks section of the TLI COC:

- other TLI#
- relevant information about condition received
- conversations with client
- other relevant information

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CREATING THE TLI CHAIN OF CUSTODY

TLI SOP No. SMC114 Version: 2	Date Written: January 16, 1996

PAGE 1 of 1

Custody Seal : Absent/Not Intact Chain of Custody : Absent Sample Tags : Absent Sample Tag Numbers : Not Listed on Chain of Custody SMO Forms : Absent	TLI Project Number		Book
	Client:		
	Date Received	By	Page
Box	Temp	Carrier and Number	

TLI Number Client ID	Matrix Location	To LAB Date/Init	To STORAGE Date/Init	To LAB Date/Init	To STORAGE Date/Init	To LAB Date/Init	To STORAGE Date/Init	To LAB Date/Init	To STORAGE Date/Init

Receiving Remarks: PLEASE READ CLIENT'S NOTE HIGHLIGHTED IN YELLOW AND SO.

Archive Remarks:

--TRIANGLE LABORATORIES OF RTP, INC.--CHAIN OF CUSTODY--REVISED 09/13/93--

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SAMPLE STORAGE AND HANDLING

TLI SOP No.	SMC120 Version: 1	Effective Date:	[illegible]
Author:	John Guenther	Date Written:	February 12, 1998
Authorization:	Phil Albro Management	Date Authorized:	3/19/98

I. **PURPOSE:** To describe the storage locations to be used following sample receipt.

II. **SCOPE:** This SOP provides instructions for determining where samples shall be stored after being received and inspected. The procedures described in this SOP are applicable to the samples received in the Environmental and Pharmaceutical Divisions.

III. **SAFETY CONSIDERATIONS:** If observing/handling samples in the Sample Custodian area, cold storage area, or laboratory area, wear appropriate personal protective equipment. This may include gloves, lab coat, and safety glasses. For additional safety information, consult the Safety and Health Officer or the "Safety and Health Manual".

IV. **PROCEDURES:**

Determination of Location

A. The Sample Custodian determines the storage locations based on the sample matrix and the analysis required by the client. See table 1 for storage locations and requirements.

B. Prior to MILES login, the Sample Custodian reviews the clients, paperwork (chain of custody, purchase order, letter, etc.) to determine the matrix and analysis requested. If the information on the client paperwork is unclear, the Sample Custodian will contact the appropriate Project Scientist for instructions prior to assigning a storage location for the samples.

C. If the samples require more than one analysis, they should be stored based on the most restrictive method requirements (e.g.: if one analysis requires refrigeration while the other can be stored at room temperature, the samples should be stored in a refrigerator/walk-in cooler).

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SAMPLE STORAGE AND HANDLING					
TLI SOP No.	SMC120	Version:	1	Date Written:	February 12, 1998

D. In some cases all the analytical methods will have the same storage requirements. The storage location selected should then be the one most convenient to the laboratory performing the analysis, if possible. See Table II for a list of possible storage locations.

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SAMPLE STORAGE AND HANDLING					
TLI SOP No.	SMC120	Version:	1	Date Written:	February 12, 1998

TABLE I

SAMPLE COLLECTION, PRESERVATION & HOLDING TIME INFORMATION

Analysis	Volume Recommended	Preservation	Storage Locations	Temperature	Holding Time
Method 624, 8240A, 8260A	2X40 ml, glass vials with Teflon septa, no headspace present	Cool, 4°C. HCl to pH<2 $Na_2S_2O_3$ if residual chlorine present (10mg/40ml sample)	R26 or R27	4±2°C	14 Days
Method 1624	3x40 ml, glass vials with Teflon septa, no headspace present	Cool, 4°C. HCl to pH<2 $Na_2S_2O_3$ if residual chlorine present (10mg/40ml sample)	R26 or R27	4±2°C	14 Days
Method 625, 8270A	2.0 L in glass bottles	Cool, 4°C, $Na_2S_2O_3$ if residual chlorine present (80mg/1L)	C02	4±2°C	7 Days to extraction; 40 days to analysis
Method 680	2.0 L in glass bottles	Cool, 4°C. $NaOH/H_2SO_4$ to pH 5-9	C02	4±2°C	7 Days to extraction; 40 days to analysis
Method 608, 8080A	2.0 L in glass bottles	Cool, 4°C. $Na_2S_2O_3$ if residual chlorine present (80mg/1L)	C02	4±2°C	7 Days to extraction; 40 days to analysis
Method 8290	2.0 L in glass bottles	Cool, 4°C. $Na_2S_2O_3$ if residual chlorine present (80mg/1L)	C01 or C02	4±2°C	30 Days to extraction; 40 days to analysis
Method 8280	2.0 L in glass bottles	Cool, 4°C	C01 or C02	4±2°C	30 Days to extraction; 40 days to analysis
Metals	0.5L in glass or plastic bottle	HNO_3 to pH<2	Metals Lab	Room Temperature	28 days Hg; 6 months all other metals
AOX/TOX	250 mL in glass bottle	HNO_3 to pH<2, $Na_2S_2O_3$ if residual chlorine present (20mg/250mL)	R05	4±2°C	no less than 3 days from collection, no more than 6 months
Method 300	250 mL in glass bottle	Cool, 4 °C	R03	4±2°C	48 Hours
Method 26/26A, Method 9056/9057	250 mL in glass bottle	None	IC Table Bay 3	Room Temperature	28 Days

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Method 0013, 218.6	250 mL in glass bottle	Cool, 4 °C	R03	4±2°C	24 Hours
Method 613	2.01 L in glass bottles	Cool, 4°C, $Na_2S_2O_3$ if residual chlorine present (80mg/1L)	C01 or C02	4±2°C	7 days to extraction; 40 days to analysis
Method 1613A	2.01 L in glass bottle	Cool, 4°C, $Na_2S_2O_3$ if residual chlorine present (80mg/1L)	C01 or C02	4±2°C	1 year to extraction; 40 days to analysis
Method 8330	50 mL or 1 L in glass bottle	Cool, 4°C	C02	4±2°C	7 days to extraction, 40 days to analysis

II. Soil, Solid, Tissue Matrices:

Analysis	Volume Recommended	Preservation	Storage Location	Temperature	Holding Time
Method 8240A	20 g, glass vials with Teflon septum, no headspace present	Cool, 4 °C	R26 or R27	4±2°C	14 Days
Method 8270A	100 g in glass jar	Cool, 4 °C	C02	4±2°C	14 Days to extraction; 40 days to analysis
Method 680	100 g in glass jar	Cool, 4 °C	C02	4±2°C	14 Days to extraction; 40 days to analysis
Method 608, 8080	100 g in glass jar	Cool, 4 °C	C02	4±2°C	14 Days to extraction; 40 days to analysis
Method 8290	100 g in glass jar (see note 5)	Cool, 4 °C	C01 or C02	4±2°C	30 days to extraction; 40 days to analysis
Metals	50 g in glass jar	none	Metals Lab	Room Temperature	28 days Hg; 6 months all other metals
AOX/TOX	50 g in glass jar	none	R05	4±2°C	no less than 3 days; no more than 6 months
Method 8330	50 g in glass jar	Cool, 4 °C	C02	4±2°C	14 days to extraction, 40 days to analysis

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TABLE II

Abbreviations:

R = Refrigerator

R/F = Refrigerator/Freezer

F = Freezer

C = Walk-in Cooler

Bay	Storage Location
3	R/F3A, R22, R/F5, IC Table
4	R3B, R/F3. R/F21A
7	R/26, R/27
8	FD
9	C02, R25, FB, FC, FE, FF, F02B, F03B, F05B, F06B
10	C01, R200
11	F30, F06, F07, F08, F20, Metals Lab
12	F11, R/FA

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